MECHANISTIC, MODEL COMPOUND, AND COPOLYMERIZATION STUDIES OF THE 4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONE RING SYSTEM

By

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This dissertation is dedicated to my brother Earl whose accomplishments, both in our profession and in everyday life, constantly set my personal goals.

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Abstract of Dissertation Presented to the
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August, 1973

Chairman: Dr. George B. Butler
Major Department: Chemistry

While the high reactivity of 4-substituted-1,2,4-triazoline-3,5-diones has been studied extensively, little work has been done to probe its utility in copolymerizations; thus, the major goals of this research have been to investigate model compound reactions of triazoline-diones that exhibit potential for copolymerizations, and to study the copolymerizations themselves.

4-Phenyl-1,2,4-triazoline-3,5-dione (PhTAD) had been observed to copolymerize with vinyl ethers and other electron rich monomers yielding one to one, alternating copolymers via a 1,4-dipole coupling mechanism. The reactions of PhTAD with seven additional electron rich comonomers were studied by this author, and the experimental data obtained in formation of the low molecular weight copolymers allowed refinement of the proposed mechanism.

PhTAD had also been observed to react with vinyl acetate to yield 1-formyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione by means of a 1,4-dipole intramolecular rearrangement. The mechanism of this rearrangement was exhaustively studied by this author by reacting

PhTAD with five new vinyl esters varying the size and electronic stabilizing ability of the vinyl ester substituents. Steric blocking decreased the relative yield of the trisubstituted triazoline-diones producing substituted 1,3,5-triazabicyclo[3.2.0]hepta-2,4-diones by closure of the 1,4-dipole, and copolymers by a mechanism similar to that suggested for the PhTAD and vinyl ether copolymerizations. Kinetic measurements were made on these reactions, and they were found to be second order overall, first order in each reactant. In comparison with the PhTAD/vinyl acetate reaction, electronic stabilization or destabilization of the 1,4-dipole respectively increased or decreased the reaction rates of the other reactions. The energies and entropies of activation were also calculated from the kinetic data, and these quantities also lent additional support to the proposed mechanism.

In an attempt to employ the 1,4-dipole intramolecular rearrangement as a means of propagation in copolymerization, divinyl and diisopropenyl adipate were reacted with bis-(p-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)-methane and a new bis-triazoline-dione synthesized by this author, 1,6-hexane-bis-1,2,4-triazoline-3,5-dione. The copolymerizations produced approximately ten percent of the desired copolymer and eighty percent of an insoluble solid which was not completely characterized.

Previous studies suggested that the reaction of styrene and bis-(p-3,5-dioxo-1,2,4—triazolin-4-ylphenyl)-methane yielded an alternating, high molecular weight copolymer. The repeat unit was thought to result from a Diels-Alder reaction followed by an ene reaction. This copolymerization was reinvestigated, and the copolymer's spectra were compared with the spectra of model compounds, which were

synthesized by the reaction of two moles of PhTAD with styrene. The comparison revealed that two types of repeat units existed in the copolymer, one ensuing a Diels-Alder reaction followed by an ene reaction, the other resulting from two consecutive Diels-Alder reactions. The repeat units were present in a two to one ratio, respectively.

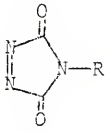
Another Diels-Alder ene copolymer was prepared by the reaction of 1,6-hexane-bis-1,2,4-triazoline-3,5-dione with styrene, and was characterized by comparison of its spectra with those of analogous model compounds. The model compounds were synthesized by reacting two moles of 4-methyl-1,2,4-triazoline-3,5-dione with styrene. The structure of the Diels-Alder ene model compound was exhaustively characterized including deuterium labelling studies.

CHAPTER I

Introduction

A. General Background

4-Substituted-1,2,4-triazoline-3,5-diones, 1, (TAD), a ring system first synthesized in 1894 by Thiele,[1] possess an extremely reactive nitrogen double bond capable of a wide variety of reactions. The



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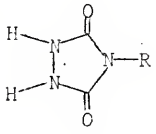

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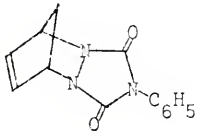
compound is generated via oxidation of the corresponding urazole, 2, a reaction which may be affected by oxidation with a number of different reagents. Thiele[1] used lead peroxide in cold, dilute sulfuric acid to yield 4-phenyl-1,2,4-triazoline-3,5-dione, and other chemists have had varying degrees of success with heavy metal salts of the urazole in reaction with iodine,[2] t-butyl hypochlorite in acetone,[3] lead tetraacetate in methylene chloride,[4] bromine,[5] fuming nitric acid,[6] and manganese dioxide, calcium hypochlorite or N-bromosuccinimide.[7] Stickler and Pirkle[8] reported the most effective oxidation, however, accomplished by passing dinitrogen tetroxide gas through a slurry of the urazole precursor in methylene chloride. Purification is achieved by solvent evaporation and sublimation.

Although a number of triazoline-diones have been prepared in this fashion, the parent compound, R=H, has never been isolated. Stolle[2] synthesized but did not isolate it in 1912, and, more recently, de Amezua, Lora-Tamayo, and Soto[9] trapped it with several dienophiles via the Diels-Alder reaction.

The chemistry of triazoline-diones - with the exception of their enhanced reactivity - is similar to that of diethylazodicarboxylate and other α-carbonyl azo compounds.[10-20] Investigations into their chemistry were begun in earnest early in the 1960's when Cookson, Gilani, and Stevens[3] published low temperature 4+2 cycloadditions of 4-phenyl-1,2,4-triazoline-3,5-dione, 3, (PhTAD) with cyclopentadiene, butadiene, and cycloheptatriene to yield 4, 5, and 6, respectively.



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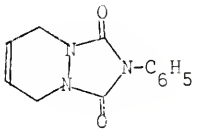

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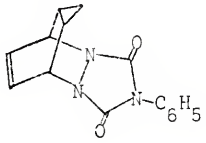

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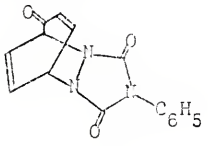
This paper initiated an extensive amount of research concerning Diels-Alder reactions of triazoline-diones.[21-26] Other cycloadditions include the reaction of PhTAD with tropone, azepine, and diazepine which produced 1:1 adducts 7, 8, and 9, respectively.[27] Evin and



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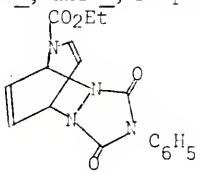

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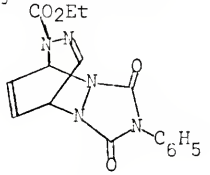

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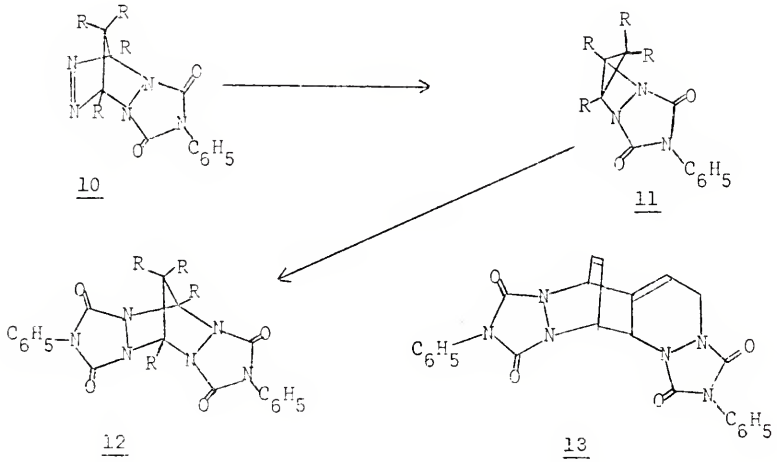
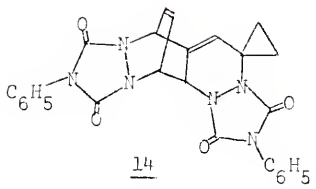
Arnold[28] have shown that isopyrazoles react with PhTAD affording structures such as 10, which can be irradiated, resulting in loss of nitrogen leading to 11. PhTAD then reacted further with 11 to give the 2:1 adduct, 12.[29] Addition to a cyclopropane ring fused in a



10 11 12 13

five membered bicyclic system had been demonstrated previously by reaction of PhTAD with bicyclo[2.1.0]-pentan-5-spiro-cyclopropane.[30] Cookson, Gilani, and Stevens[31] also reported a 2:1 adduct, 13, of PhTAD with styrene, presumably the result of a double Diels-Alder reaction. Other 2:1 adducts have been observed, such as 14, the product of PhTAD and benzylidenecyclopropane[32] and the 1:1 adduct of PhTAD and oxonin, 15, which adds another PhTAD to give a 2:1 adduct of unknown structure.[33, 34, 35]

Other investigations of Diels-Alder cycloadditions include reactions of PhTAD with 5-iodocyclopentadiene which gave 16,[36] and with polyenic azonines that produced compounds structured as 17.[37]



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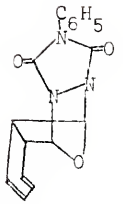

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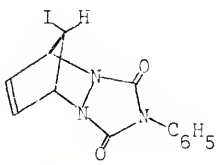

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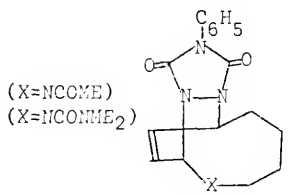

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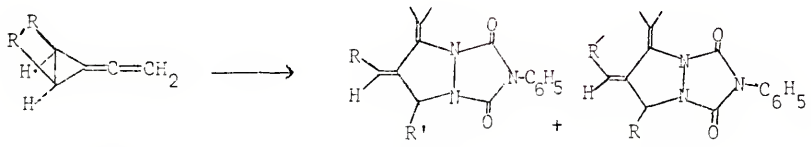
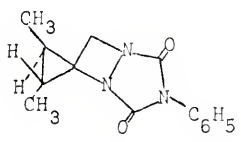
As previously mentioned, triazoline-diones contain an extremely reactive ring system, especially in cycloaddition conversions. Kinetic studies have shown PhTAD to be one of the most powerful dienophiles known to date.[38] PhTAD, in reaction with 2-chloro-1,3-butadiene, was found to react one thousand times faster than tetracyanoethylene and some two thousand times faster than maleic anhydride.

Cycloadditions of triazoline-diones are not limited to Diels-Alder reactions as recent studies show. Pasto and Chen[39] observed a $((\alpha^2+\pi^2)+\pi^2)$ cycloaddition of alkenylidenecyclopropanes, 18, and PhTAD affording 19 and 20. Other cycloadditions of PhTAD and alkenylidenecyclopropanes have been reported more recently.[40] trans-2,3-Dimethylmethylenecyclopropane reacts with PhTAD at room temperature to yield the 2+2 cycloaddition adduct, 21.[32] These



18 19 20

authors have also observed cycloaddition reactions of substituted vinyl cyclopropanes with PhTAD.[41] Von Gustorf and coworkers[42]



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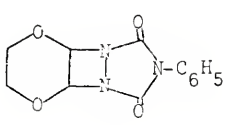
found PhTAD to react in a 2+2 fashion with dihydro-1,4-dioxime yielding 22, and with indene giving 23. The indene reaction pathway was thought to be polar in nature, as the proposed 1,4-dipole was trapped with water.



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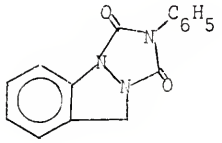

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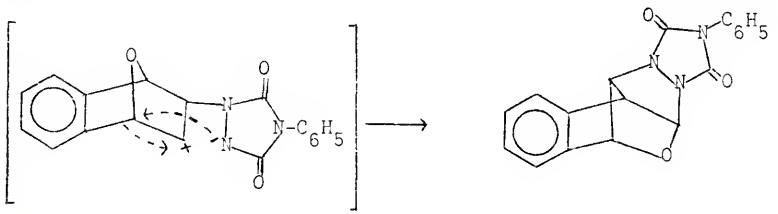
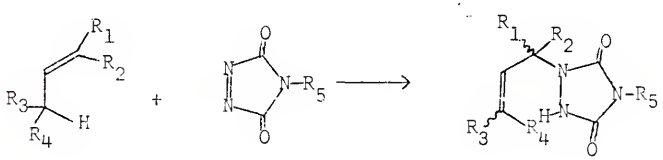
The presence of an ionic reactive intermediate was also noted in the addition of PhTAD to oxabenzonorbornadiene yielding 24, which underwent a Wagner-Meerwein alkyl shift and ring closure to 25.[43]

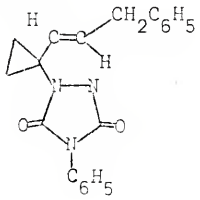


24 25

Another type of reaction pathway available for triazolinediones is the Diels-ene conversion (shown below). Pasto and Chen[32] observed



the ene product, 26, in the reaction of (4-phenylbutylidene)-cyclopropane and PhTAD. Pirkle and Stickler[44] also investigated the ene reaction and found PhTAD to be thirty thousand times more reactive than ethylazodicarboxylate in reaction with a number of monoolefins having α-hydrogens.



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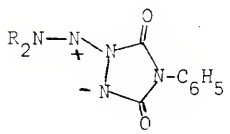

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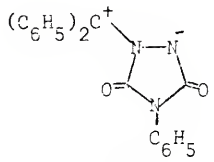
Cookson and coworkers[45] have reported the oxidation of alcohols to aldehydes and ketones with PhTAD. Substituted hydrazines also have been oxidized by PhTAD affording an N-nitrene, which reacted with a second PhTAD to yield an azimine, 27.[46,47] Oxidation of benzophenone hydrazone yielded an N-nitrene which reacted with PhTAD! as before, but the azimine produced was unstable. Nitrogen was evolved forming 28 which reacted further with benzophenone hydrazone to give the azine, 29.[48]



28

$(C_6H_5)_2-C=N-N=C-(C_6H_5)_2$

29

PhTAD has been used in the synthesis of prismane by initial reaction with benzvalene, followed by basic hydrolysis and then photolysis.[49]

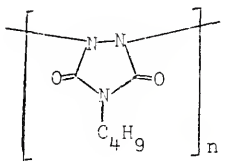
PhTAD has also been reported to be a useful ligand in iridium complexes.[50]

B. Research Objectives

While the high reactivity of the triazoline-dione ring system has been investigated extensively as a monofunctional molecule, few attempts have been made to utilize this high reactivity as a propagating mode in polymerization; thus, the main objectives of this study have been:

1. To investigate model compound reactions of triazoline-diones that exhibit potential for copolymerization.
2. To attempt the copolymerizations themselves.

Pirkle and Stickler[51] homopolymerized 4-butyl-1,2,4-triazoline-3,5-dione in chlorinated solvents by photolyzing the solution with a visible light source (150 watt quartz-iodine tungsten lamp). The polymer was thought to have a repeat unit 30 and a degree of polymerization of twenty.



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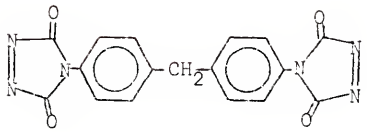
Depolymerization of the polymer in solution resulted, however, upon removal of the irradiating source regenerating 73% of the monomer; for this reason, further studies of the homopolymers were not contemplated, even though the thermal stability could be enhanced by end-capping the polymer with diazomethane.

Saville[52] has studied the reaction of bis-(p-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)-methane, 31, with a solution of natural rubber



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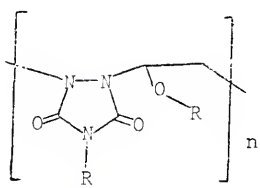
and observed crosslinking due to the occurrence of the ene reaction; however, the high reactivity of 31 prevented its use as a uniform crosslinking agent of dry, unextended rubber.

Butler, Guilbault, and Turner[53] investigated the reaction of triazoline-diones with vinyl ethers and discovered the formation of low molecular weight, alternating copolymers containing repeat units



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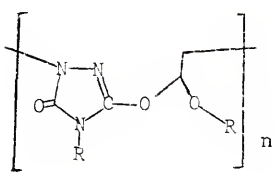

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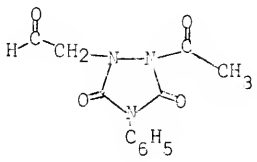
32 and 33 via a 1,4-dipole coupling mechanism. When alkyl ketones were used as solvents for the reaction, the 1,4-dipoles were trapped yielding a new oxadiazine ring system.[54] Guilbault, Turner and Butler[55] also synthesized polymers having backbones of similar molecular structure by reacting PhTAD with N-vinyl carbamates. Further studies of these copolymerizations were planned - specifically to refine the proposed mechanism and to characterize the new copolymers - and has been a primary objective of this study.

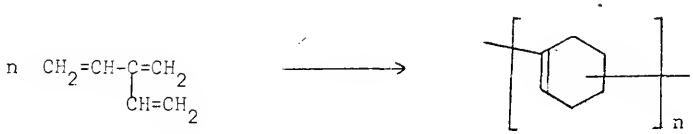
In addition, Turner[56] found that, in reaction with vinyl acetate, PhTAD yielded a 1,4-dipole which underwent intramolecular rearrangement to yield 1-formyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione, 34. An exhaustive study of this rearrangement was proposed,



34

and reactions were planned using the rearrangement as a propagation mode for copolymerization.

In the past, few Diels-Alder reactions have been used successfully in polymerizations. 2-Vinylbutadiene, 35, undergoes self-addition yielding an insoluble polymer.[57] α,α'-Bis(cyclopentadienyl)p-xylene, 36, also undergoes self-addition in benzene yielding soluble polymers.[57]



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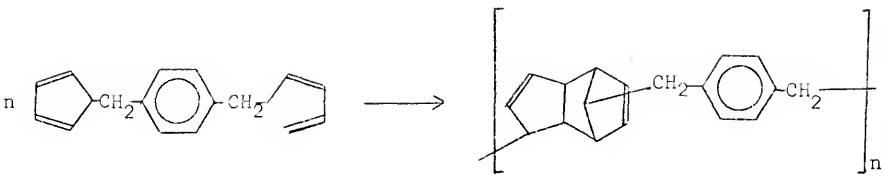

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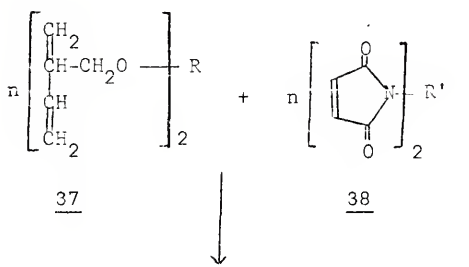
Step-growth copolymerizations of a bidiene with a bidienophile have also been studied, such as the copolymerizations of several bidienes, 37, prepared from 2-hydroxymethylbutadiene, with N,N'-bis-(maleimides), 38, yielding copolymers of low intrinsic viscosity.[58] The major



37 38

drawback of most of these and other Diels-Alder polymerizations is the fact that the yields and reaction conversions are inherently low. Propagations by the Diels-Alder reaction can be classified as step-growth mechanism, addition polymerizations; thus, molecular weights

are governed by the Carothers Equation (Equation 1). The average degree of polymerization, $\overline{DP}$, is a function of the reaction conversion, p, and a conversion of 98% or greater is necessary for high molecular weights.

Equation 1 $$\overline{DP} = \frac{1}{(1-p)}$$

This requirement severely limits polymerization by the Diels-Alder reaction. Attempts to increase conversion by raising the temperature usually initiates a retro-Diels-Alder reaction, which results in depolymerization. Since triazoline-diones are extremely reactive dienophiles, it was thought that their use might result in high conversions at relatively low reaction temperatures; thus, model compound reactions and copolymerizations were planned with the objective of obtaining high molecular weight copolymers.

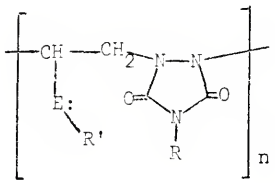
CHAPTER II

Results and Discussion

A. 1,4-Dipole Copolymers

Review of previous results

Recently G.B. Butler, L.J. Guilbault, and S.R. Turner prepared low molecular weight, alternating copolymers by the reaction of 4-substituted-1,2,4-triazoline-3,5-diones with vinyl monomers containing electron donating groups adjacent to the double bond.[53] These copolymers, listed in Table I, were described as containing both repeat units 39 and 40, with 39 predominating when the electron



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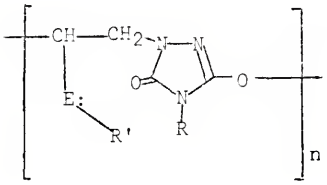

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donating ability of "E" was large. Repeat unit 40 - identified by its strong infrared band at 1610 cm.$^{-1}$ due to the -C=N- linkage - isomerized to 39 if heated or allowed to stand in solution. The copolymers were soluble in most organic solvents, and were white, odorless solids softening around 100°. Yields were generally greater than 80%. Catalytic hydrogenation of the divinyl ether/PhTAD copolymer yielded a copolymer having the same nuclear magnetic

Table I [59]

Summary of the 1,4-Dipole Copolymers

Prepared by Turner, Guilbault and Butler[a]

Comonomer	Product	$\bar{M}_n$[b] (Range)[c]
Divinyl Ether	1:1 copolymer	(450-3100)
Ethyl Vinyl Ether	1:1 copolymer	(410-3900)
Isobutyl Vinyl Ether	1:1 copolymer	-
Divinyl Carbonate	2:1 copolymer	1240
N-Vinyl Carbazole	1:1 copolymer	(3000-5000)[d]
N-Vinyl Carbamate	1:1 copolymer	4400

[a]Copolymerizations carried out in methylene chloride. Other solvents were also studied.

[b]Analysis by vapor pressure osmometry.

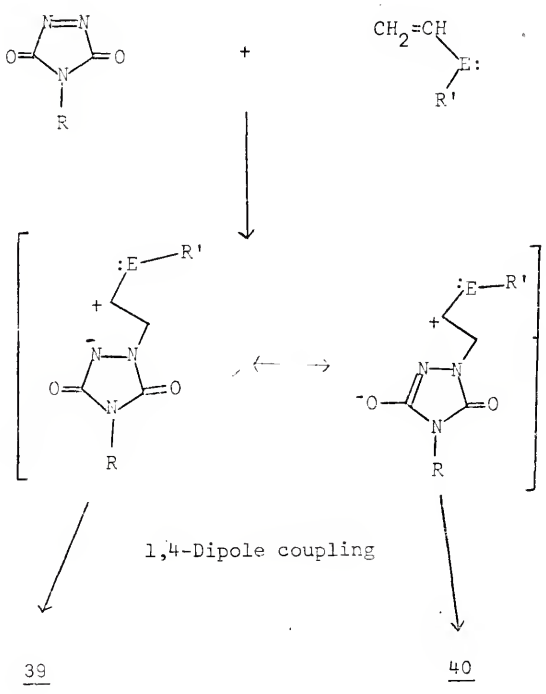
[c]Large number of samples prepared.

[d]Analysis by gel permeation chromatography, S.R. Turner, Private Communication, Xerox Corporation.

resonance chemical shifts as observed for the ethyl protons in the ethyl vinyl ether/PhTAD copolymers.

The copolymerizations occurred spontaneously at room temperature and were thought to proceed via coupling of a dipolar intermediate (Scheme I). When the copolymerizations of PhTAD and ethyl vinyl ether (EVE), divinyl ether (DVE), or isobutyl vinyl ether (IVE) were completed using acetone as the solvent, a small percentage of the proposed 1,4-dipole was trapped by the carbonyl yielding the corresponding tetrahydrooxadiazines.

SCHEME I



The 1,4-dipole copolymers were either formed exclusively or as a mixture of copolymer and the corresponding 1,3,5-triazabicyclo-[3.2.0]hepta-2,4-dione (commonly referred to as a 1,2-diazetidine), depending upon the electron donating ability of the group adjacent to the vinyl group of the vinyl comonomer. For example, the reaction of PhTAD and ethyl vinyl ether afforded copolymer exclusively, while the divinyl ether/PhTAD reaction yielded a mixture of the 1,2-diazetidine and copolymer. These results were attributed to the greater stability of the ethyl vinyl ether/PhTAD 1,4-dipole relative to the divinyl ether/PhTAD 1,4-dipole, whose stability was decreased (and reactivity increased) by the electron withdrawing vinyl group. The divinyl ether/PhTAD 1,2-diazetidine could be converted to copolymer by heating a methylene chloride solution to 60°.

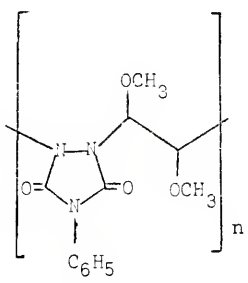
The N-vinyl carbamate/PhTAD reaction[55] also yielded a 1,2-diazetidine along with an alternating 1:1 copolymer; however, the 1,2-diazetidine was thermally stable, even at 60°. The ring could be opened to copolymer chemically by hydrolyzing the amide function to the amine with gaseous HBr, after which polymerization occurred.

Three possible methods of termination which would lead to low molecular weight copolymers were proposed. Since the propagating species were thought to be ionic, impurities such as water could easily have terminated the chain. Dipolar coupling would also terminate the chain leading to a macrocycle. Thirdly, disproportionation between two chains would lead to a vinyl ether end group and a urazole end group concluding growth of both chains.

Preparation of new copolymers

Further studies of 1,4-dipole copolymers were completed by this author, and Table II describes additional copolymers resulting from the reaction of vinyl monomers and PhTAD.

Equimolar quantities of 1,2-dimethoxyethylene (80% trans) and PhTAD reacted spontaneously at room temperature resulting in an 80% yield of a white, odorless solid. Spectral and elemental analysis indicated the solid to be polymeric in nature with repeat units 42 and 43 present, 43 predominating as confirmed by the strong 1610 $cm.^{-1}$ band in the infrared spectrum. Further analysis of the reaction revealed a 12% yield of a white, odorless adduct whose elemental



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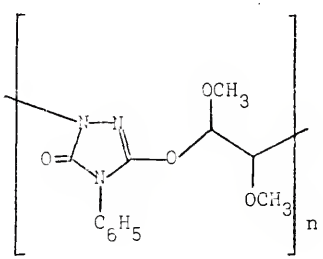

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and nuclear magnetic resonance analysis indicated the presence of a 1,2-diazetidine ring structure. Upon heating a solution of the adduct in tetrahydrofuran to 60°, the 1,2-diazetidine ring apparently opened to a low molecular weight, alternating copolymer. Analysis as before showed the predominating repeat unit to be 43.

p-2-Vinyloxyethoxytoluene reacted rapidly with PhTAD giving an 85% yield of a crystalline, white copolymer of low molecular weight. Nuclear magnetic resonance and infrared analysis indicated the predominance of repeat unit 44, since the 1610 $cm.^{-1}$ band was

Table II

Additional 1,4-Dipole Copolymers[a]

Comonomer	Product	$\overline{M}_n$[b] (Range)
1,2-Dimethoxyethylene (80% trans)	1:1 copolymer	1860
p-2-Vinyloxyethoxy toluene	1:1 copolymer	1430
N-Vinyl-2-pyrrolidone	1:1 copolymer	1100
N-Vinylsuccinimide	1:1 copolymer	1400
Vinyl Benzoate	> 1:1 copolymer[c]	1200
Vinyl Isobutyrate	> 1:1 copolymer[c]	1250
Vinyl Pivalate	> 1:1 copolymer[c]	(1230-1500)

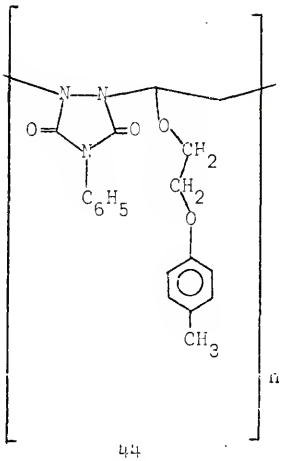
[a]Methylene chloride used as solvent.

[b]Analysis by vapor pressure osmometry.

[c]Copolymerizations at 60°; > 1:1 indicates larger percentage of PhTAD.

very weak in the infrared spectrum.

The reactions of 1-vinyl-2-pyrrolidone and N-vinyl succinimide with PhTAD were both rapid, room temperature copolymerizations each yielding approximately 85% 1:1 alternating copolymers, the former mostly structured as 45, the latter as 46.



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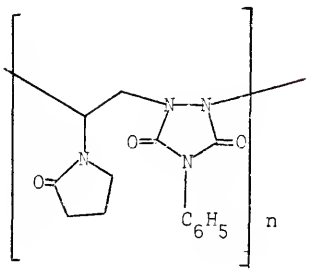

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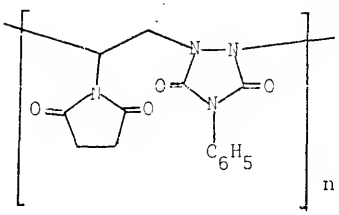

46

Since the 1610 cm.$^{-1}$ band was very weak for both copolymers, the repeat unit containing the -C=N- linkage was thought to be present only in low percentages.

Contrary to the PhTAD reactions of vinyl ethers and compounds having vinylic groups adjacent to amide-like nitrogens, vinyl esters reacted very slowly at room temperature - in one case, not at all - and in some instances, adducts resulted exclusive of copolymer formation. While the details of adduct formation are discussed in section "B" of this chapter, their copolymers are described here in comparison with the other 1,4-dipole copolymers. Vinyl benzoate, vinyl pivalate,

and vinyl isobutyrate formed low molecular weight copolymers in yields of 87%, 16%, and 15%, respectively, in addition to adduct formation, while isopropenyl acetate and vinyl chloroacetate afforded adducts only. Due to the low reactivity of the vinyl esters, the reactions were carried out at 60° in a sealed tube. Even at this temperature, vinyl trifluoroacetate failed to react. Although elemental analysis of the copolymers disclosed a larger percentage of PhTAD present, indicating the copolymers were no longer alternating, the infrared and nuclear magnetic resonance spectra were similar to the spectra of the 1:1 alternating copolymers; thus it was thought that the repeated units in each case were similar to those previously reported.

Refinement of the mechanism proposed by Turner, Butler, and Guilbault

In an attempt to more closely compare the new results with those already published by Turner, Guilbault, and Butler, the following equation* was used to determine the molar ratio of comonomers in the 1,4-dipole copolymers:

Equation 2 $$\frac{n_1}{n_2} = \frac{E_2M_2 - E_AM_2}{E_AM_1 - E_1M_1}$$

M_1 and M_2 are the molecular weights of PhTAD and vinyl ester, respectively; E_1 and E_2 represent the percent of the element present (C, H, or N) in PhTAD and vinyl ester, and E_A represents the percent element (C, H, or N) obtained from the elemental analysis. The comonomer ratio of PhTAD to vinyl ester in the copolymer, n_1/n_2,

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* Derived by Mr. J. Wrobel, Department of Chemistry, University of Florida.

was calculated for each carbon, hydrogen and nitrogen analysis, and the average value, $\overline{n_1/n_2}$, is reported in Table III. The products of reactions 1 through 8 are most likely formed via an identical intermediate, which probably differs in some fashion from the intermediate involved in reactions 9 through 12. Experimental evidence has shown a 1,4-dipole to be involved in both types of copolymers since both dipoles have been trapped by acetone;[60] however, the reactivity of the 1,4-dipole is apparently influenced by the stabilizing ability of the electron pair of the atom adjacent to the positive charge.

With the above thoughts in mind, a modified mechanism for the Turner et al. reaction of PhTAD and ethyl vinyl ether is proposed in Scheme II, which can be taken as a specific example for the general formation of 1:1 alternating copolymers. Ethyl vinyl ether reacts with PhTAD generating the initial 1,4-dipole, 47, which can either couple with another nearby 1,4-dipole or close to the 1,2-diazetidine, 48. The 1,2-diazetidine can open to generate low concentrations of 1,4-dipole to "feed" the 1,4-dipole coupling process leading to copolymer. The ease of opening of the 1,2-diazetidine is affected by the electron pair adjacent to the positive center; in this case, the ring opening is facile under reaction conditions. The overall reaction of the 1,4-dipole is depicted in the energy diagram below, demonstrating the 1,2-diazetidine to be the kinetically favored product of the reaction and the copolymer, the thermodynamically stable product.

At room temperature, the 1,2-diazetidine rapidly opens to form copolymer; however, if the reaction temperature is lowered to -9°,

Table III

Molar Ratios for 1,4-Dipole Copolymers[a]

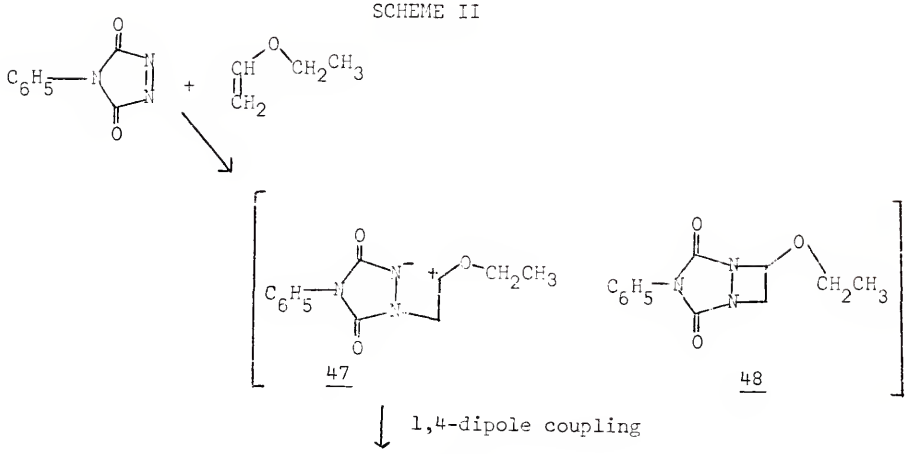
Reaction No.	Comonomer	Reaction Temperature	$\overline{n_1/n_2}$
1	Divinyl Ether	RT	1.01/1
2	Divinyl Ether	60°	1.03/1
3	Ethyl Vinyl Ether	RT	1.07/1
4	1,2-Dimethoxyethylene	RT	0.975/1
5	p-2-vinyloxyethoxytoluene	RT	1.00/1
6	N-vinyl-2-pyrrolidone	RT	1/1[b]
7	N-vinylsuccinimide	RT	1.08/1
8	N-vinyl Carbazole	RT	0.910/1
9	Vinyl Benzoate	60°	1.32/1
10	Vinyl Benzoate	RT	1.27/1
11	Vinyl Pivalate[c]	60°	1.72/1
12	Vinyl Isobutyrate	60°	2.01/1

[a]Copolymerizations 1, 2, 3, and 8 were completed by Turner, Guilbault, and Butler.

[b]Carbon analysis not included.

[c]Sample prepared and analyzed twice to insure accuracy.

SCHEME II



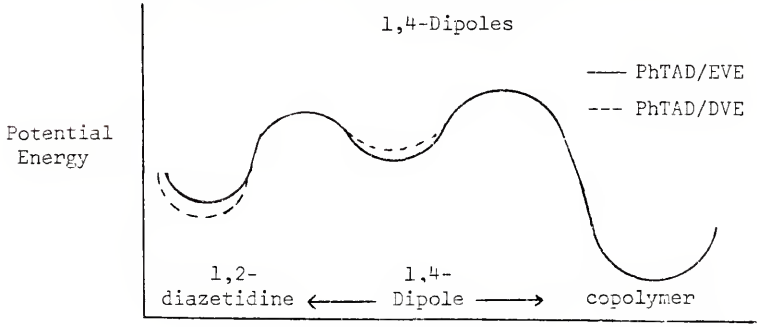
47 48

1,4-dipole coupling

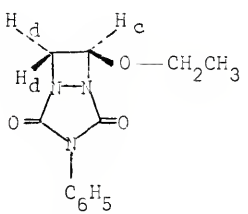
1:1 Copolymer

the 1,2-diazetidine can be observed by nuclear magnetic resonance analysis as described following. Equimolar quantities of PhTAD and EVE in methylene chloride were mixed in a nuclear magnetic resonance tube at -10°, which was then placed in the spectrometer. The temperature was regulated to -9°, and the first scan of the colorless solution, which contained mostly 1,2-diazetidine, 49 and some copolymer, produced a triplet at δ1.48 (protons "a" as assigned in 49), a multiplet centered at δ4.0 (presumably "b" - poor resolution prevented quartet assignment), a multiplet centered at δ4.65 (protons "c"), a triplet at δ5.80 (proton "d"), and a singlet at δ7.65 (protons "e"). The solution was warmed to +2°, and continuous sweeps were made to witness changes in the nuclear magnetic resonance pattern. Over a period of 30 minutes, the kinetically favored 1,2-diazetidine opened to form copolymer, resulting in broadening of the methyl, methylene, and phenyl signals while

Energy Diagram for Reaction of PhTAD/EVE and PhTAD/DVE



the CH_2 signal at δ4.65 and the CH signal at δ5.80 were lost, due to disappearance of the 1,2-diazetidine ring structure. The broadening of signals due to copolymerization is demonstrated in Figure 1, which illustrates how the aromatic singlet changes with time.



49

As previously mentioned, Turner et al., observed two products in the DVE/PhTAD reaction, the 1,2-diazetidine and the copolymer. In this instance, the kinetically favored product is more stable than the EVE/PhTAD 1,2-diazetidine, as shown in the same energy diagram. This is due to the decreased donating ability of the electron pair on oxygen in divinyl ether, which inhibits the opening of the 1,2-diazetidine.

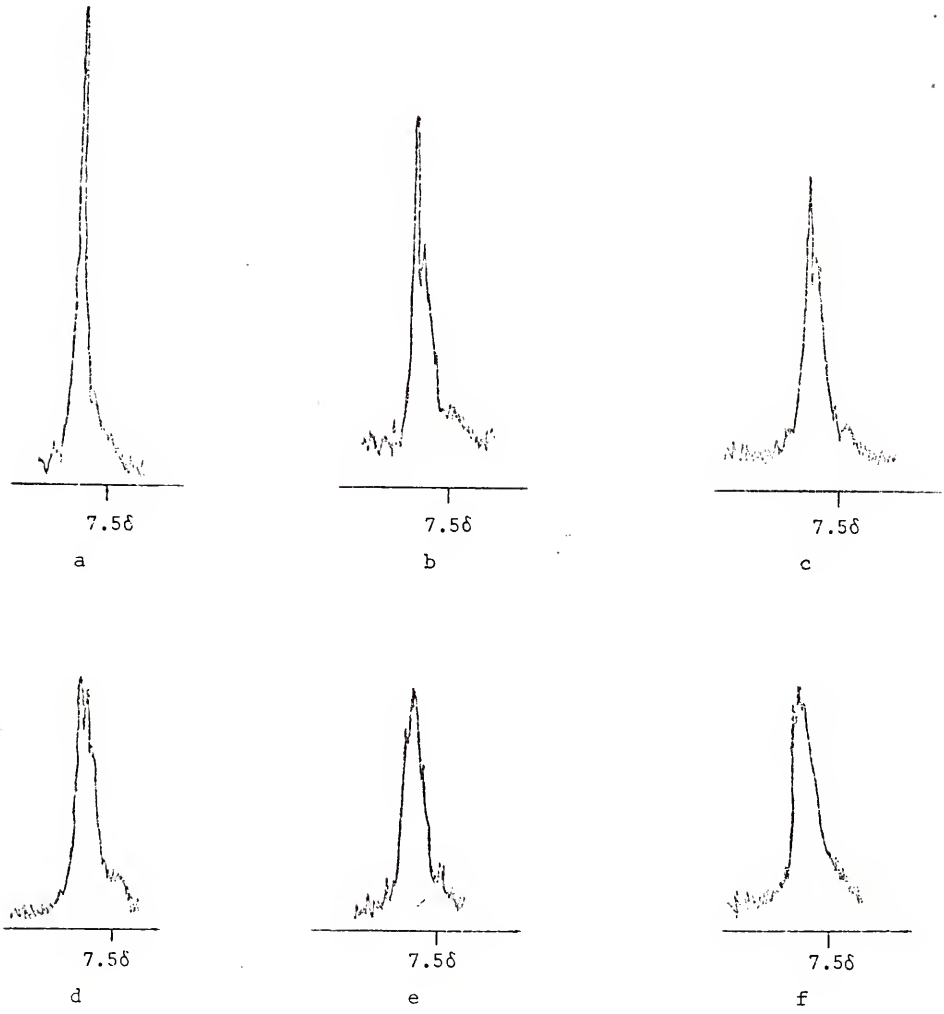


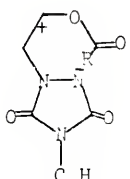
Figure 1

Aromatic Singlet of 49 As It Opens To Copolymer

Readings at five-minute intervals, "a" through "f"; first reading at -9°, all others at +2°. Note the growth of a new, broadened singlet slightly upfield, which can be assigned to the copolymer.

In the PhTAD/N-vinyl carbamate reaction, the 1,2-diazetidine is no longer kinetically favored. Once it is formed, it remains thermally stable, and the amount generated relative to copolymer is dependent upon the activation energies of each step. Guilbault and Butler's[55] results show the ratio of copolymer to 1,2-diazetidine to be 1.9/1, indicating the activation energy for 1,2-diazetidine formation is greater than that for copolymer formation.

In the reactions of vinyl esters (reactions 9-12, Table III), the 1,4-dipole, 50, is more energetic (less stable), relative to the 1,4-dipoles previously discussed, due to the decreased stability of the positive center. This is a result of lowered resonance sharing of the ester oxygen's electron pair. The more energetic 1,4-dipole,



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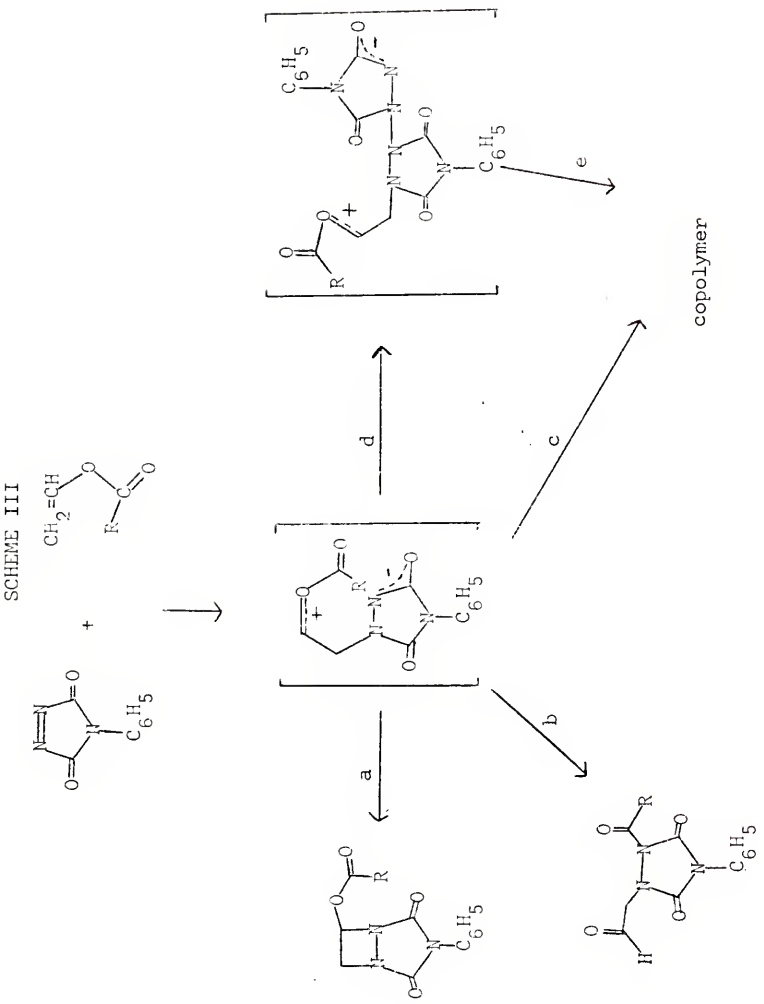
manifested in its dramatically slower rate of formation, can participate in other reactions as well, as is exemplified in Scheme III. The 1,4-dipole apparently has four options, each controlled by each pathway's activation energy. The 1,4-dipole may either couple to yield alternating copolymer (path "a") or close to 1,2-diazetidine (path "b") as before. Two new reactions appear to be occurring also, intramolecular rearrangement (path "c", discussed in Section "B" of this chapter), and nucleophilic attack on another molecule of PhTAD

SCHEME III



(path "d"), giving 51, leading to copolymer (path "e"). The 1,2-diazetidines are thermally stable at 60°; thus, the energy picture for this route parallels that of the formation of the PhTAD/N-vinyl carbamate 1,2-diazetidine.

PhTAD is known to slowly decompose at 60° (10% conversion after 24 hours)[61] and probably accounts for a part of the greater than 1:1 PhTAD/vinyl ester comonomer molar ratio. However, the rate of decomposition is not large enough to completely explain the high molar ratios; the balance of the increase in the ratios for these copolymers could be accounted for by nucleophilic attack by the 1,4-dipole on another molecule of PhTAD (path "d"). Experimental evidence is consistent with this hypothesis. Table IV lists the comonomer molar ratios, calculated using equation 2, for the PhTAD/vinyl benzoate (VB) copolymerizations as both the comonomer feed ratio and the temperature are changed. Note that the ratio increases as the feed ratio (PhTAD/VB) increases. The ratio also increases as the reaction temperature increases, which is consistent with the activation energy of path "d" being greater than path "c".

Table IV

Comonomer Molar Ratios for Vinyl Benzoate Copolymerizations

Feed Ratio (PhTAD/VB)	Temperature	n_1/n_2
1:1	RT	1.27/1
10:1	RT	2.37/1
1:1	60°	1.32/1
10:1	60°	2.82/1

While the structures of these copolymers are not identical to that of the other 1,4-dipole copolymers, they appear to be at least similar in structure, having broadened nuclear magnetic resonance signals and almost identical infrared spectra. The 1610 $cm.^{-1}$ is present for all three copolymers, suggesting the presence of the -C=N- linkage in the repeat unit.

Methods of termination of the propagating 1,4-dipoles are assumed to be the same as those proposed for the one-to-one alternating copolymers.

B. The 1,4-Dipole Intramolecular Rearrangement

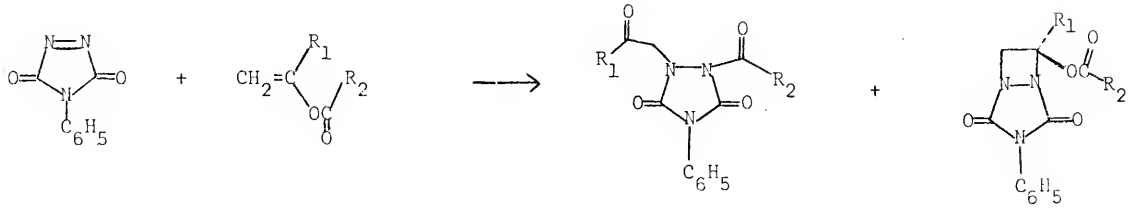
Reactions of PhTAD and vinyl esters

As mentioned in Chapter I, Turner and Butler[56] found the reaction of PhTAD and vinyl acetate to yield an adduct, 34, by means of an intramolecular rearrangement of the 1,4-dipole, instead of the expected copolymer. While cycloaddition reactions of 1,4-dipoles are well documented, intramolecular rearrangements of these dipoles have rarely been observed.[62] In an attempt to clearly define the mechanism of the PhTAD/vinyl acetate reaction, a variety of vinyl esters were reacted with PhTAD varying the size and the electronic stabilizing ability of the substituents. The results of these reactions are shown in Scheme IV.

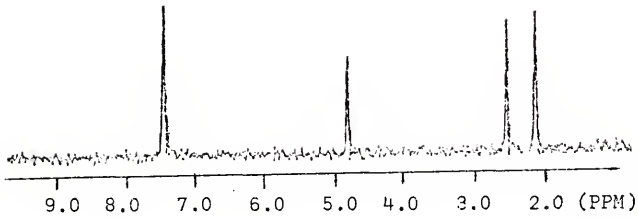
Equimolar quantities of PhTAD and isopropenyl acetate, 52, reacted in methylene chloride at 60° yielding 1-acetylmethyl-2-phenyl-1,2,4-triazoline-3,5-dione, 53, exclusively. The infrared spectrum and the elemental analysis were consistent with the assigned structure. In Figure 2, the nuclear magnetic resonance spectra of 34 and 53 are compared. Note that when isopropenyl acetate is used as a reactant instead of vinyl acetate, the methyl signal of 53 replaces the aldehyde signal of 34 while the other signals remain in the same positions. Nuclear magnetic resonance data for these and the other products of the PhTAD/vinyl ester reactions may be found in Table V.

Vinyl chloroacetate, 54, reacted with PhTAD producing 1-formylmethyl-2-chloroacetyl-4-phenyl-1,2,4-triazoline-3,5-dione, 55, exclusively. Structural assignment was based upon the product's nuclear magnetic resonance spectrum, elemental analysis, and its infrared spectrum,

SCHEME IV

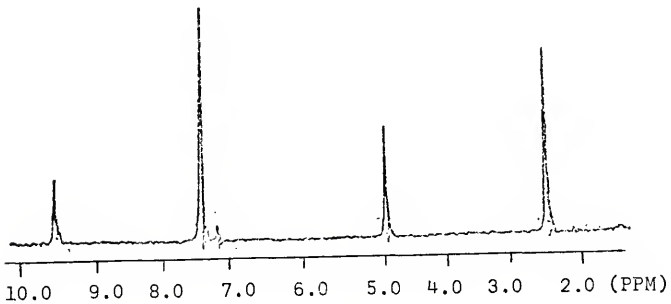


	R_1	R_2		R_1	R_2		R_1	R_2
52	CH_3	CH_3	53	CH_3	CH_3			
54	H	CH_2Cl	55	H	CH_2Cl			
56	H	C_6H_5	57	H	C_6H_5	58	H	C_6H_5 + polymer
59	H	$CH(CH_3)_2$	60	H	$CH(CH_3)_2$	61	H	$CH(CH_3)_2$ + polymer
62	H	$C(CH_3)_3$	63	H	$C(CH_3)_2$	64	H	$C(CH_3)_2$ + polymer



"a"

spectrum of 53



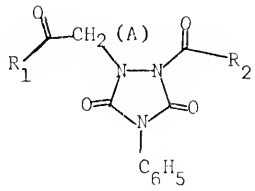
"b"

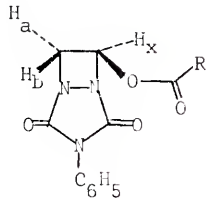
spectrum of 34^{63}

Figure 2

Comparison of Nuclear Magnetic Resonance Spectra of 51 and 34

Table V [a] Nuclear Magnetic Resonance Data for the Vinyl Ester/PhTAD Reactions





Compd.	R_1	R_2	A
53	2.10(s,3)	2.52(s,3)	4.78(s,2)
55	9.60(s,1)	4.97(s,2)	4.72(s,2)
57	9.66(s)	b	4.78(s)
60	9.57(s,1)	4.15(m,1) 1.25(d,6)	4.79(s,2)
63	9.53(s,1)	1.37(s,9)	4.63(s,2)

Compd.	R	H_a	H_b	H_x	J_{AB}	J_{AX}	J_{BX}
58	b	4.20[c](m)		6.19(m)			
61	2.54(d,6) 2.23(d,6)	4.58(q,1)	4.29(q,1)	6.56(q,1)	10	6	5
64	1.20(s,9)	4.60(q,1)	4.27(q,1)	6.49(q,1)	10	6	5

[a] In chloroform-d_1 with 1% TMS as internal standard. Values reported in δ units. N-phenyl protons appeared in 7.41-7.50δ region for all compounds. Abbreviations used are: s=singlet, d=doublet, q=quartet, m=multiplet.

[b] Complex multiplet absorption in the 7.2-7.8δ region was observed for the two phenyl groups.

[c] Complex absorption pattern for both protons.

which exhibited weak aldehyde bands at 2880 and 2745 cm.$^{-1}$ and strong carbonyl bands at 1810 and 1730 (broad) cm.$^{-1}$.

Vinyl benzoate, 56, yielded three products in reaction with PhTAD. 1-Formylmethyl-2-benxoyloxy-4-phenyl-1,2,4-triazoline-3,5-dione, 57, resulted in low yield, its structure ascertained by nuclear magnetic resonance analysis. 3-Phenyl-6-benzoyloxy-1,3,5-triazabicyclo[3.2.0] hepta-2,4-dione, 58, was formed in low yield, and structural assignment was also based upon nuclear magnetic resonance analysis. The major product of the reaction was a low molecular weight copolymer, discussed in section "A" of this chapter.

Vinyl isobutyrate, 59, also afforded three products in reaction with PhTAD, but the major product was 1-formylmethyl-2-(2-methyl-propionyl)-4-phenyl-1,2,4-triazoline-3,5-dione, 60, instead of the 1,4-dipole copolymer. The infrared spectrum of 60 exhibited weak aldehyde bands at 2870 and 2750 cm.$^{-1}$ and carbonyl bands at 1800, 1735 (broad), and 1720 cm.$^{-1}$. Nuclear magnetic resonance and elemental analysis also supported assignment of structure. The third product of the reaction, 3-phenyl-6-(2-methylpropionyloxy)-1,3,5-triazabicyclo-[3.2.0] hepta-2,4-dione, 61, produced three strong carbonyl bands in the infrared spectrum at 1780, 1755, and 1720 cm.$^{-1}$, corresponding to the three carbonyls present in the adduct. Elemental analysis and nuclear magnetic resonance analysis (in comparison with the nuclear magnetic resonance spectra of other 1,2-diazetidines recorded by von Gustorf, et al.[42]) also supported the structure.

The vinyl pivalate, 62, /PhTAD reaction yielded 1-formylmethyl-2-(2,2-dimethylpropionyl)-4-phenyl-1,2,4-triazoline-3,5-dione, 63,

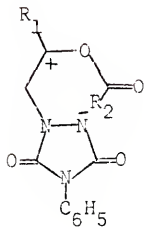
and 3-phenyl-6-(2,2'-dimethylpropionyl)-1,3,5-triazabicyclo[3.2.0] hepta-2,4-dione, 64, along with a low yield of copolymer. The products were identified by infrared, nuclear magnetic resonance, and elemental analysis as before.

With the exception of 53, all of the trisubstituted 1,2,4-triazoline-3,5-diones were substituted acetaldehydes. Normally, the aldehyde proton is observed to couple with the adjacent methylene.[64] These aldehydes, however, exhibited no coupling at all. A sample of 34 was subjected to nuclear magnetic resonance analysis from -20° to 80°, and no coupling was observed; use of a 100 MHz spectrometer also produced no coupling. The methine proton of the analogous acetal - 1-(1,1-diethoxy-2-ethyl)-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dione - did exhibit coupling (δ4.80, triplet, j=2 Hz.), but the coupling constant was smaller than those observed for similar acetals.[65] Apparently, the phenomenon that prevents coupling of the aldehyde proton in 34 also lowers the coupling constant of the corresponding acetal.

In general, the yields for the PhTAD/vinyl ester reactions were greater than 85%. Mass spectra were made for all products having nuclear magnetic resonance data, and the molecular ion was detected in each case.

Mechanistic aspects of the reaction

A plausible mechanism for these reactions involves a 1,4-dipole, 65, as the reactive intermediate, formed via initial reaction of the electron rich double bond of the vinyl ester with the electron poor



65

nitrogen, nitrogen double bond. The 1,4-dipole, once formed, undergoes intramolecular nucleophilic attack by nitrogen on the carbonyl carbon displacing the ester oxygen (path "a", Scheme V).

Intramolecular nucleophilic attack by nitrogen is sterically hindered by large R_2 groups, decreasing the relative yield of the rearrangement product (Table VI); thus, while the 1,4-dipoles formed

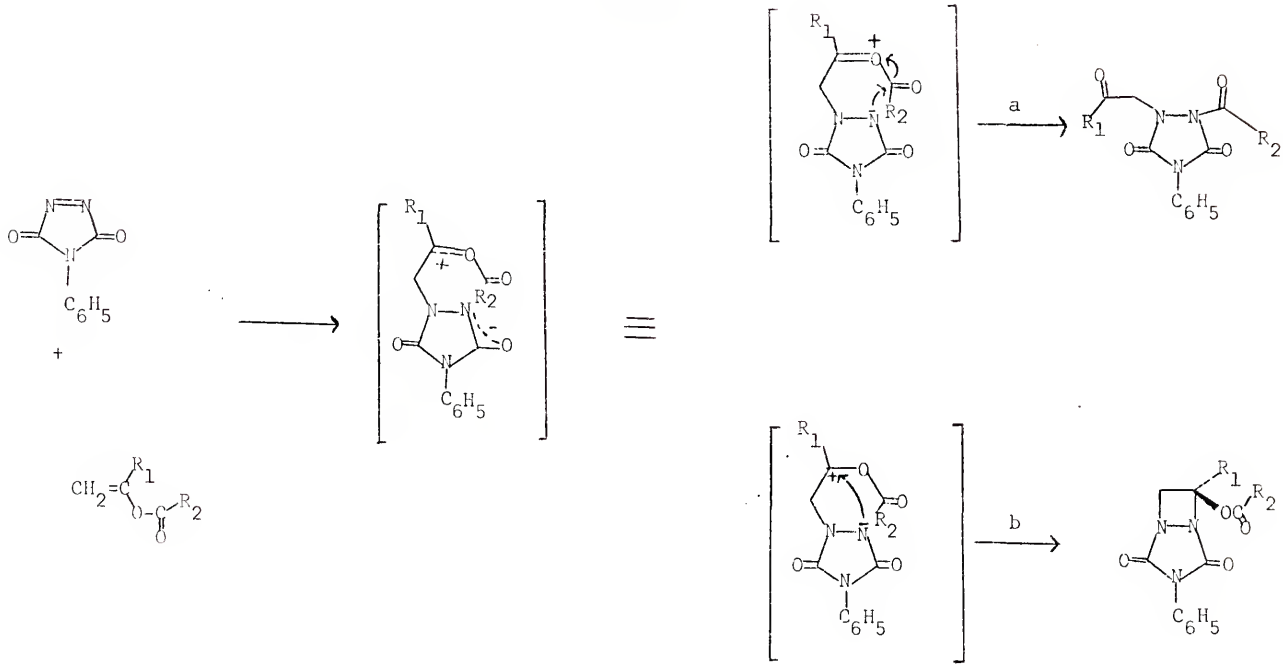
Table VI

Relative Yields of Products

Ester	Rearrangement Product (%)	1,2-diazetidine(%)	Copolymer (%)
52, 54	100	0	0
59	77	8	15
62	42	42	16
56	6	7	87

in the reaction of 52 and 54 with PhTAD rearrange exclusively, the dipoles of 56, 59, and 62 yield two other products as well, 1,3,5-

SCHEME V



triazabicyclo[3.2.0] hepta-2,4-diones by path "b", Scheme V, and copolymers by the mechanism discussed in section "A" of this chapter.

A third mechanistic possibility - reaction through an acylium ion - can be eliminated on the basis of two reactions listed in Table VI. A highly unstable chloroacylium ion would be required as the reactive intermediate in the reaction of 54 with PhTAD. Also, 56 reacts with PhTAD to give copolymer as the major product, contrary to what would be expected (i.e., a high yield of 57) if a benzacylium ion were the reactive intermediate.

In an attempt to obtain kinetic and thermodynamic data supporting the existence of the proposed 1,4-dipole, the reactions were studied spectroscopically monitoring PhTAD's visible absorbance at 545 nanometers. Assuming irreversibility, the reactions were found to be second order overall and first order in each reactant. Table VII lists the second order rate constants at 60° along with the energies of activation, calculated by the Arrhenius method,[66] and the entropies of activation, calculated using equation 3.[67]

Equation 3

$$\Delta S_a = \left(\ln k - \ln \frac{\kappa T}{h} + \frac{\Delta E_a}{RT} - 1\right)$$

ΔS_a = entropy of activation
k = 2nd order rate constant
κ = 1.38 X 10^{-16} erg $deg.^{-1}$
h = 6.62 X 10^{-27} erg sec.
R = 1.99 ℓ/mol. sec.
ΔE_a = energy of activation

A large, negative entropy of activation is often observed for reactions involving a charged transition state. For example, the reaction of aniline and bromoacetophenone is thought to proceed via a charged transition state, shown below, and has an entropy of activation of -50 cal/deg. mol.[68] The PhTAD/vinyl ester reactions

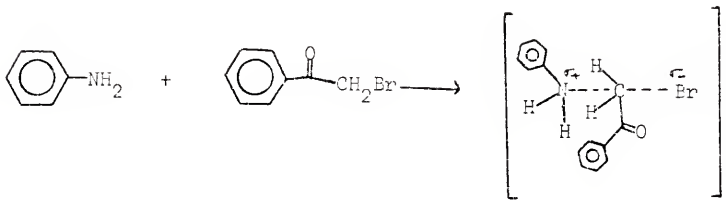
Table VII[a,b]

Kinetic and Thermodynamic Data for the Vinyl Ester/PhTAD Reactions

Ester	R_1	R_2	k	ΔE_{act}	ΔS_{act}
Isopropenyl Acetate	CH_3	CH_3	2.7×10^{-1}	7.4 (0.977)	-41
Vinyl Acetate	H	CH_3	4.2×10^{-2}	12	-32
Vinyl Isobutyrate	H	$CH(CH_3)_2$	5.9×10^{-2}	12 (0.977)	-32
Vinyl Pivalate	H	$C(CH_3)_3$	4.0×10^{-2}	12	-31
Vinyl Chloroacetate	H	CH_2Cl	8.1×10^{-4}	14 (0.997)	-30
Vinyl Benzoate	H	C_6H_5	4.3×10^{-2}	11 (0.988)	-34

[a]The coefficient of correlation was calculated for the rate constants and the energies of activation and is reported in parentheses. If no value is shown in the table, the coefficient of correlation is 0.999 or better.

[b]The units for the rate constant "k" are ℓ/mol-sec. The units for the activation energy are Kcal/mol, and for the entropy term, cal/mol-degree.



closely parallel this situation, and the relatively large negative values for the entropies of activation are consistent with a charged transition state leading to a 1,4-dipole, since an increase in the order of the system results from adduct formation and solvent attraction to the charged species.

The size of R_2 has no effect on the energy of activation as shown by the R_2:alkyl series. This is indicative of an intermediate being formed, followed by nucleophilic attack effecting rearrangement. Since the relative yield of the intramolecular rearrangement product decreases as the size of R_2 increases (Table VI), the product ratios must be determined by the activation energies in the second step of the mechanism, the intramolecular rearrangement. The possibility of product formation occurring from other than a common intermediate was considered, i.e., formation of the intramolecular rearrangement product and copolymer by opening of the 1,2-diazetidine ring. This pathway was eliminated by determining the 1,2-diazetidine to be thermally stable under the reaction conditions employed.

The ease of formation of the 1,4-dipole is directly affected by the inductive effects of R_1 and R_2. Changing R_1 from a methyl group to a hydrogen increases the activation energy 4 1/2 kcal/mol., demonstrating the importance of cation stabilization. The 1,4-dipole is destabilized further by placing a chloromethyl group at R_2, a phenomenon analogous in the opposite sense to the increase of the acidity of chloroacetic over acetic acid. The activation energy for the vinyl benzoate reaction is slightly lower than for the R_2= alkyl series, possibly due to conjugation of the ester carbonyl with the aromatic ring allowing increased lone pair sharing by the ester oxygen. The failure of vinyl trifluoroacetate to react with PhTAD can be attributed to the destabilizing electronic effect of the three fluorines. Apparently, the activation energy required for formation of the 1,4-dipole is too large to be overcome at 60°; thus, no reaction is observed at this temperature.

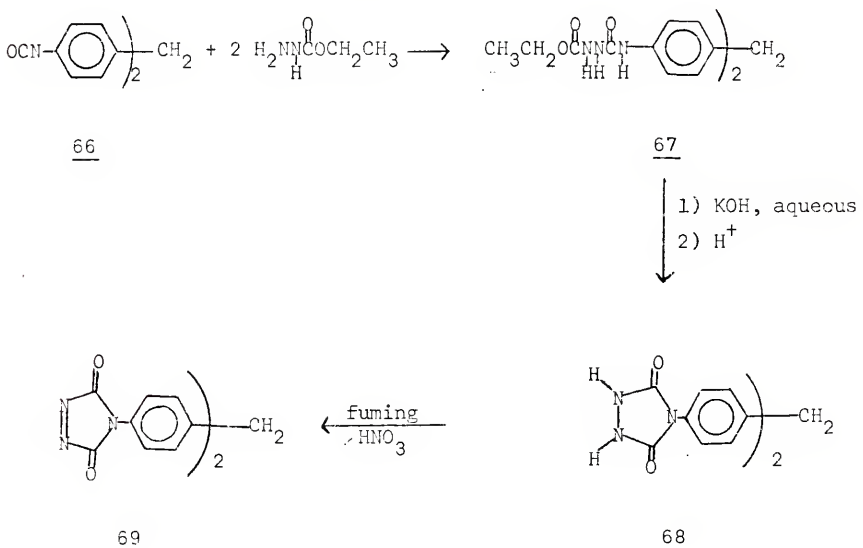
C. Bis-Triazoline-Dione Copolymerizations

Synthesis of bis-triazoline-diones

Two bis-triazoline-diones were used in this study, one prepared using procedures developed by Saville[52] and Turner,[69] and the other by modification of these procedures.

Bis-(p-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)methane, 69, was prepared by the sequence of steps illustrated in Scheme VI.[52] One mole of bis-(4-isocyanatophenyl)methane, 66, reacted with two moles

SCHEME VI



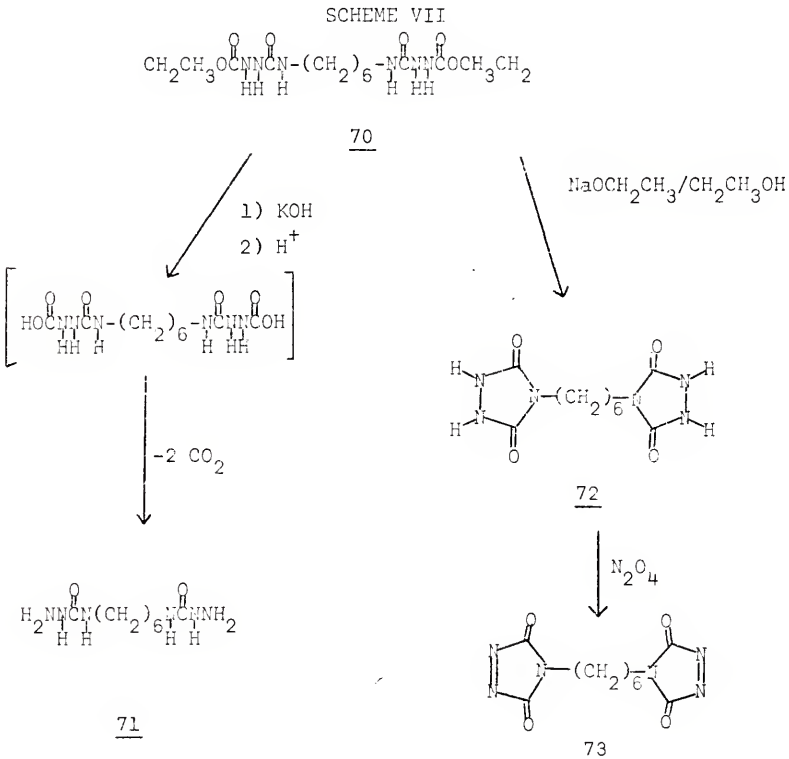
66 67 69 68

of ethyl carbazate yielding the bis-semicarbizide, 67. Cyclization of this bis-semicarbizide was achieved by slowly adding the solid to a 2M solution of potassium hydroxide, followed by neutralization and

filtration of the bis-urazole, 68. Oxidation to the desired bis-triazoline-dione, 69, was done using fuming nitric acid.

1,6-Hexane-bis-1,2,4-triazoline-3,5-dione, 73, was prepared in a similar fashion and is shown in Scheme VII. The corresponding

SCHEME VII



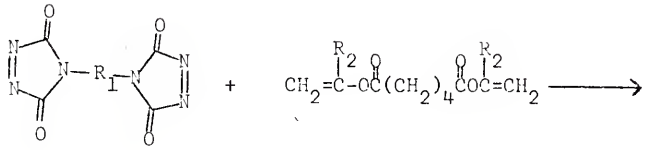
bis-semicarbizide, 70, was prepared as before; however, attempted cyclization in either aqueous or alcoholic 2M potassium hydroxide led to hydrolysis of the ester function followed by decarboxylation - detected by infrared analysis of the CO_2 evolved - giving the proposed structure, 71. The cyclization was achieved by refluxing

70 in a sodium ethoxide/ethanol solution overnight, followed by filtration of a light tan solid. Since the light tan solid was extremely water soluble and had a high melting point, it is likely that it existed as the sodium salt of the diurazole. Oxidation of the tan solid using dinitrogen tetroxide yielded the desired bis-triazoline-dione, 73. If the tan solid was dissolved in water and the resultant solution was neutralized with 50% HCl, a low yield of the diurazole, 72, characterized by nuclear magnetic resonance, infrared, and elemental analysis, precipitated from solution.

Copolymerizations of bis-triazoline-diones and divinyl esters of dicarboxylic acids

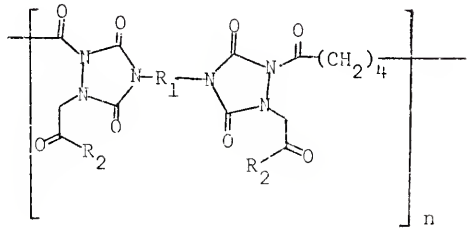
In an attempt to employ the intramolecular rearrangement discussed in section "B" of this chapter as a mode of propagation for copolymerization, 69 and 73 were reacted with diisopropenyl adipate, 74, and divinyl adipate, 75, prepared by the reaction of isopropenyl[70] and vinyl acetate[71] with adipic acid. Diisopropenyl adipate was used as a comonomer to lower the energy of activation necessary to cause copolymerization; thus, it was hoped that lower temperatures could be used for copolymerization, decreasing the possibility of copolymer degradation. Although this effect was not observed - all the copolymers characterized were of approximately the same molecular weight - the time necessary for complete reaction was decreased by a factor of two when 74 was used as a comonomer. The results of all of the copolymerizations are summarized in Scheme VIII.

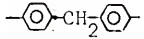
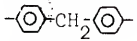
SCHEME VIII

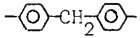
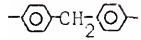


insoluble solid

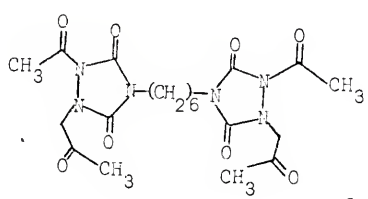
+



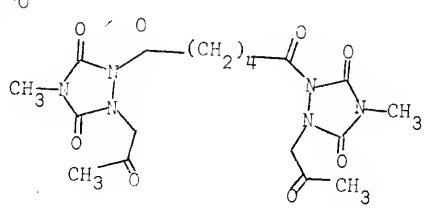
	R_1		R_2
73	$(CH_2)_6$	74	CH_3
69		75	H
69		74	CH_3
73	$(CH_2)_6$	75	H

	R_1	R_2
76	$(CH_2)_6$	CH_3
77		H
78		CH_3
79	$(CH_2)_6$	H

The copolymerization of 73 and 74 in tetrahydrofuran was studied at room temperature and 60°, and in both cases the characteristic red color of 73 discharged to light yellow while a light yellow opaque gel formed. The gel was filtered, and the filtrate was slowly added to a tenfold excess of hexane causing precipitation of an off-white solid. In both cases the yield of precipitated solid was less than 10% of the theoretical. The nuclear magnetic resonance spectrum of the precipitate gave resonance signals at δ1.5 (broad mulitplet, protons "a" in Figure III), δ1.7 (broad multiplet, protons "b"), δ2.1 (singlet, protons "c"), δ3.0 (broad multiplet, protons "d"), δ3.6 (broad multiplet, protons "e"), and δ4.8 (singlet, protons "f"). Comparison of this spectrum with the spectra of model compounds 80 - prepared in an 80% yield by reaction of 73 with two moles of isopropenyl acetate - and 81 - synthesized in a 90% yield by the reaction of 74



80



81

with two moles of 4-methyl-1,2,4-triazoline-3,5-dione - allowed the assignment of 76 as the copolymer's structural repeat unit. Infrared and elemental analysis confirmed the assignment of structure. The assignment of nuclear magnetic resonance signals to the proton type is shown in Figure 3. Vapor pressure osmometry in acetone gave a number average molecular weight of 1780.

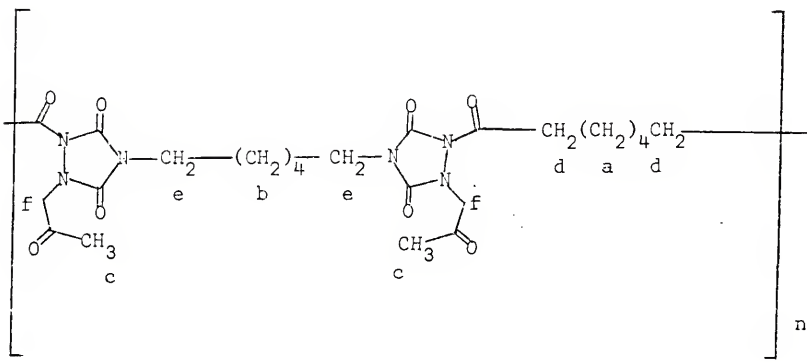


Figure 3

Assignment of Proton Type to Nuclear Magnetic Resonance Signals for 76

a, δ1.5; b, δ1.7; c, δ2.1; d, δ3.0; e, δ3.6; f, δ4.8

In both the room temperature and the 60° copolymerizations, the light yellow gel was generated in greater than 80% of the theoretical yield and was insoluble in most organic solvents. Swelling was noted in dimethylformamide and dimethylsulfoxide, however. Although the infrared spectrum was almost identical to the spectrum of the soluble copolymer, it was difficult to make a structural assignment based upon this evidence along. A sample of the solid

was heated to 60° in dimethylsulfoxide-d_6 for five hours, and about 10% of the solid was solubilized. Nuclear magnetic resonance analysis was inconclusive, however, since it was possible that copolymer degradation could have occurred under these conditions. Resonance signals at δ1.8 and δ3.6 were assigned to the solvent, tetrahydrofuran, which was apparently trapped with the copolymer. The elemental analysis was consistent with this conclusion since the carbon, hydrogen, and oxygen percentages were higher than those calculated for a 1:1 comonomer ratio in the copolymer.

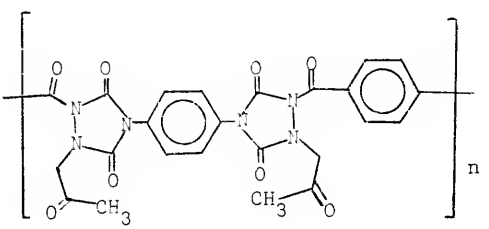
The soluble, low molecular weight copolymer, 79, resulting from the reaction of 73 and 75 in tetrahydrofuran, was also prepared at room temperature and 60°. As before, no noticeable difference was detected by increasing the reaction temperature other than decreasing the time necessary for complete reaction. The major product of the copolymerization (83%) was an insoluble gel solvated by tetrahydrofuran.

The copolymerization of 69 and 75 was attempted in tetrahydrofuran at 60° producing a 75% yield of an insoluble gel and a 12% yield of a soluble copolymer, 77. Structural assignment of 77 was based upon nuclear magnetic resonance, elemental, and infrared analysis. The insoluble gel swelled in dimethylformamide and dimethylsulfoxide, and a nuclear magnetic resonance spectrum of a sample solubilized in dimethylsulfoxide-d_6 by heating gave very broad signals from which no definitive proton assignments could be made. The copolymer was solvated by dimethylformamide as evidenced by signals at δ2.8 (doublet) and δ7.9 (broad singlet). The elemental analysis

also gave this indication. As before, the infrared spectrum was almost identical to that of the soluble copolymer.

The copolymerization of 69 and 74 in tetrahydrofuran, yielding a soluble copolymer and an insoluble solid, proceeded in a manner analogous to the formation of 76 and 77. As before, the low molecular weight, soluble copolymer, 78, was fully characterized, while conclusive assignment of a copolymer repeat unit structure for the insoluble solid was not feasible as only an infrared spectrum could be made.

With the intention of preparing a thermally stable copolymer, shown below, by reaction of diisopropenyl terephthalate and p-phenyl-bis-1,2,4-triazoline-3,5-dione, the synthesis of diisopropenyl



terephthalate was attempted. No success was achieved in reacting terephthalic acid and isopropenyl acetate using a procedure similar to that previously tried. Apparently, the insolubility of the diacid prevented reaction from occurring. Dimethyl terephthalate was used in an attempted ester exchange with isopropenyl acetate, and although the reaction medium was homogeneous and a color change was noted, the desired diester could not be isolated. No further

synthesis work was attempted, and the thermally stable copolymer was not synthesized.

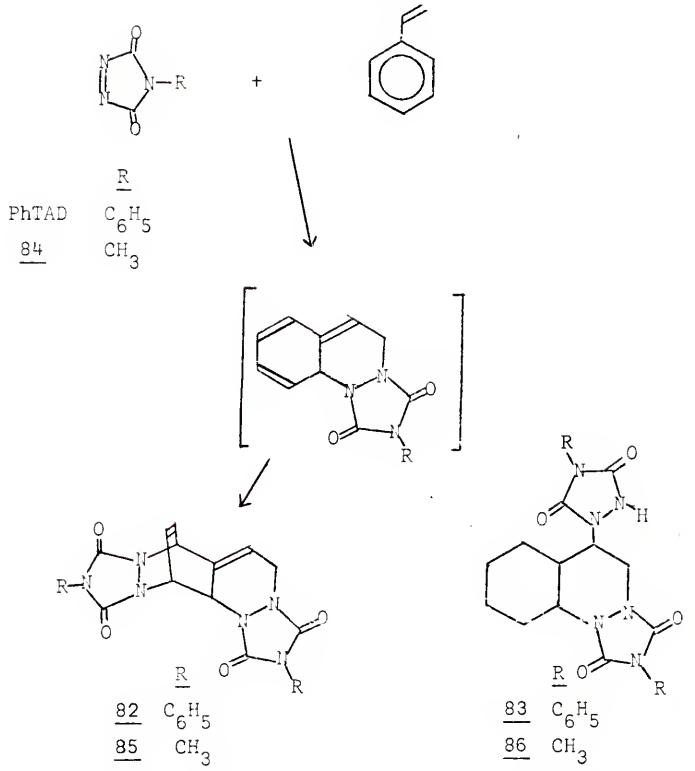
Although the insoluble copolymers were never fully characterized, it is reasonable to assume that the 1,4-dipole intramolecular rearrangement was at least one of the propagating reactions responsible for their formation. Therefore, two possibilities should be considered as explanations of the insolubility of these copolymers. Due to the high polarity of the copolymer backbone, interchain attraction would account for the intractability of the solids. If this is the case, then solution would be caused by solvation of the copolymer backbone in hot dimethylsulfoxide-d_6, replacing interchain attraction.

The other possibility would involve chemical crosslinking. That is, a reaction undetected in the intramolecular rearrangement model compound studies, possibly vinyl polymerization of vinyl ester end groups, would chemically bond the copolymer chains forming an insoluble gel. In this case, heating the copolymer in dimethylsulfoxide-d_6 would result in a chemical breakdown of the crosslink, degrading the copolymer.

Diels-Alder ene copolymerizations

Cookson, Gilani and Stevens[31] have investigated the Diels-Alder reactions of PhTAD and found, in reaction with styrene, a double Diels-Alder adduct, 82, was obtained. Reinvestigation of the reaction by this author revealed that a Diels-Alder-ene adduct, 83, was also formed, as shown in Scheme IX, in approximately a 2:1 ratio (ratio computed by nuclear magnetic resonance analysis) of 83 to 82.

SCHEME IX



Separation of the mixture by fractional crystallization yielded pure samples of both adducts, 82 being identified by comparison with the results of Cookson et al., and 83 characterized by infrared, mass spectral, elemental and nuclear magnetic resonance analysis. Deuterium exchange with the proton on nitrogen was also observed in the nuclear magnetic resonance spectrum. 4-Methyl-1,2,4-triazoline-3,5-dione, 84, also reacted with styrene yielding both products in the same approximate ratio, 2:1 of 86 to 85. Purification of 86[72] was achieved via fractional crystallization and structural assignment was based on analyses described above including ultraviolet analysis

to ascertain the presence of the reformed aromatic ring. Attempts to separate 85 from 86 by fractional crystallization and column chromatography were unsuccessful; however, its presence was assured by a detailed examination of a nuclear magnetic resonance spectrum of the mixture, in comparison with the spectrum of a pure sample of 86.

Nuclear magnetic resonance analysis of the Diels-Alder ene products disclosed a doublet around δ8.2 which has been assigned as one aromatic proton. For example, the nuclear magnetic resonance spectrum of 86 (Figure 4) exhibited a doublet at δ8.23; specific proton assignment was impossible, however, based on these data alone since it could have been either "f_1" or "f_2" in Figure 4. Unequivocal proton assignment was achieved, by reacting 84 with 3,4,5-trideuteriostyrene* by the procedure described for the reaction with styrene, resulting in the Diels-Alder ene product, 87, as one of the products. The nuclear magnetic resonance spectrum of 87 (Figure 5) showed loss of the doublet and the appearance of a singlet in the other aromatic region; thus, the doublet's proton assignment in 86 must have been "f_2", "f_1" being found in the aromatic region.

These results suggested the Diels-Alder ene reaction as a possible propagation mechanism in copolymerizations of styrene and bis-triazoline-diones 69 and 73. Both comonomers were reacted with

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* Sample provided by Dr. H.J. Harwood, The University of Akron, Akron, Ohio.

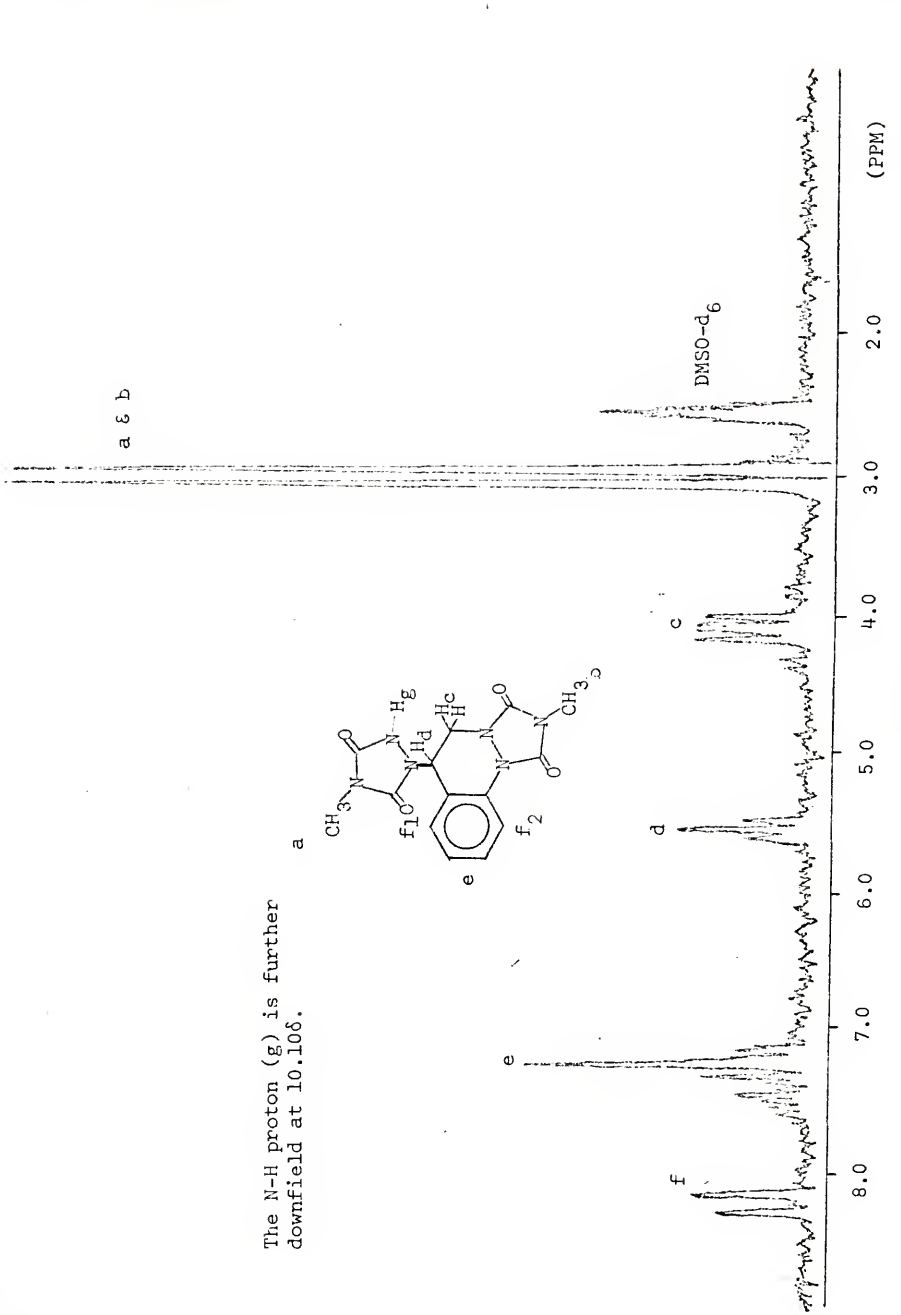


Figure 4

NMR Spectrum of 86

The N-H proton (f) is further downfield at 10.10δ.

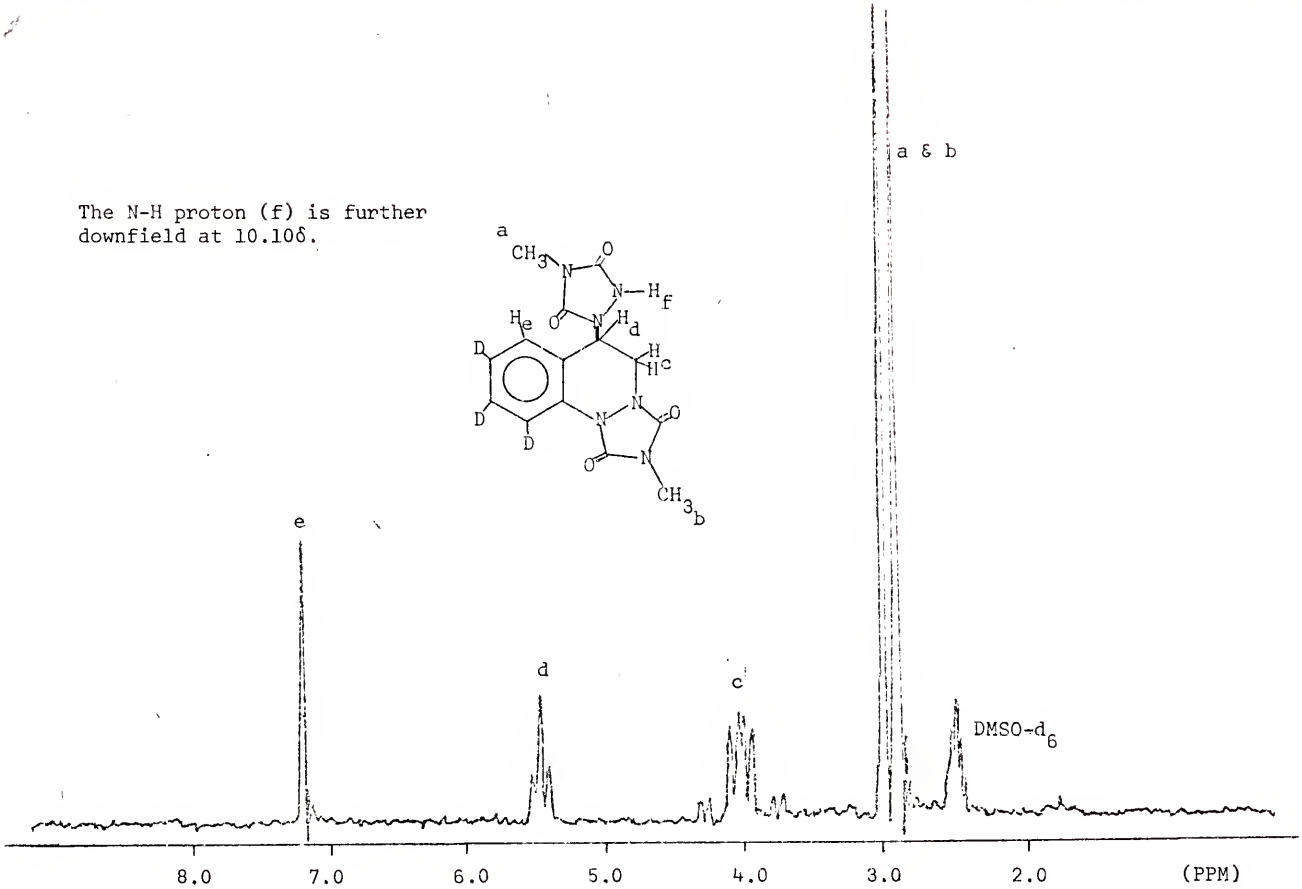
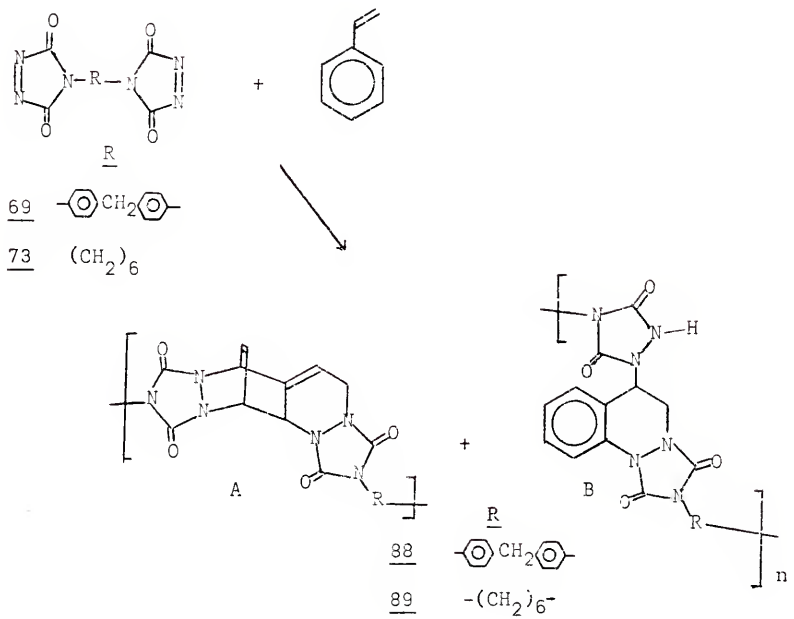


Figure 5

NMR Spectrum of 87

styrene, and the results are given in Scheme X.

SCHEME IX.



Reaction of concentrated solutions of 69 in dimethyl formamide with equimolar quantities of styrene rapidly yielded high molecular weight copolymer, 88, [η] = 0.33 dl. g. Structural assignment was based on infrared, elemental, and nuclear magnetic resonance analysis. Deuterium exchange with the proton on nitrogen was also observed in the nuclear magnetic resonance spectrum; nuclear magnetic resonance analysis did not disclose the repeat unit ratio (B:A), however, due to poor resolution of the extremely viscous nuclear magnetic resonance solution. The copolymer was soluble in dimethylformamide, dimethylsulfoxide, hexafluoroisopropanol, hexamethylphosphorictriamide, and

N-methylpyrrolidone, and insoluble in ethyl ether, tetrahydrofuran, ethyl acetate, methanol, methylene chloride, acetonitrile, benzene, acetone, nitromethane, and water.

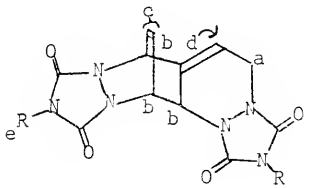
Turner[73] also investigated the copolymerization of 69 and styrene, and although a copolymer was isolated, the elemental analysis was not consistent with a 1:1 reaction of comonomer in the copolymer. The nuclear magnetic resonance spectrum of the copolymer also gave evidence of the Diels-Alder ene repeat unit ("B" in Scheme IX) being present in the copolymer, however.

Reaction of a dilute solution of 73 in methylene chloride with an equimolar quantity of styrene rapidly yielded a low molecular weight copolymer, 89, $[\eta]$ = 0.08 dl./g. Vapor pressure osmometry studies in methylene chloride gave a number average molecular weight of 2300. Structural assignment was based on analyses described for 88 including ultraviolet spectroscopy, which confirmed the presence of the aromatic ring in repeat unit "B". As before, deuterium exchange with the proton on nitrogen was noted in the nuclear magnetic resonance spectrum, and an approximate 2:1 ratio of repeat units "B" to "A", respectively, was calculated from the spectrum. The copolymer was soluble in methylene chloride, dimethylformamide, dimethylsulfoxide, chloroform, and 1,1,2,2-tetrachloroethane, and insoluble in acetone, benzene, acetonitrile, and water.

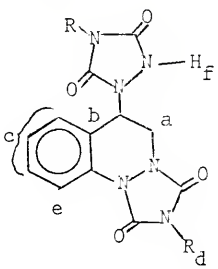
The nuclear magnetic resonance signals for the model compounds, 82, 83, 85 and 86, are reported in Table VIII, and may be compared with the signals of the copolymers, 88 and 89, listed in Table IX.

Table VIII

Nuclear Magnetic Resonance Data for the Diels-Alder Ene Model Compounds[1]



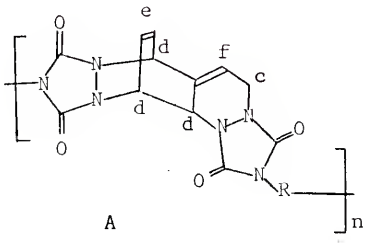
Compd.	a	b	c	d[2]	e
82	4.35(m,2)	5.63(m,1) 6.15(m,1) 6.47(m,1)	6.77(t,2) J=3.5 Hz	7.21(m)[3]	7.42(s)[3] 7.48(s)[3]
85	4.38(m)	5.58(m) 6.00(m) 6.45(m)	6.73(t) J=3.5 Hz	7.19(m)	2.89(s) 2.95(s)



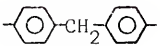
Compd.	a	b	c	d	e	f[5,6]
83	4.03(m,2)	5.43(t,1)	7.17(m)[4]	7.20(s)[4] 7.25(s)[4]	8.19(d,1) J=7 Hz	10.42
86	4.03(m,2)	5.50(t,1) J=3 Hz	7.42(m,3)	2.87(s,3) 2.98(s,3)	8.23(d,1) J=7 Hz	10.10

[1] In DMSO-d_6, 1% TMS. Values reported in δ units. Abbreviations used are a, singlet; d, doublet; t, triplet; m, multiplet.
[2] Signal partially hidden in aromatic absorption.
[3] Eleven protons total.
[4] Thirteen protons total.
[5] Very broad signal.
[6] Protons on nitrogen were found to exchange with deuterium when 1 drop of D_2O was added to the nuclear magnetic resonance tube.

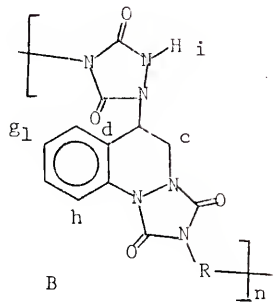
Table IX Nuclear Magnetic Resonance Data for the Diels-Alder Ene Copolymers*



A

88 R = 

89 R = $-CH_2-(CH_2)_4-CH_2-$
b a b



B

Polymer	a	b	c	d	e	f	g	h	i
88	-	-	4.19	5.59** 6.05 6.43	6.68	7.16	7.35 (g_1 & g_2)	8.21	10.40
89	1.33	3.40	4.25	5.54** 5.98 6.39	6.67	7.20	7.38 (g_1 only)	8.25 (d)	10.00

* Polymers gave poorly resolved nuclear magnetic resonance signals. Two signals were not identified, one at 3.26 in [13] and the other at 4.88 in [14]. Note that letter designations for protons in the polymers are not identical to the letter designations for protons in the model compounds.

** Signal for protons α to nitrogen in repeat unit B and one of the protons α to nitrogen in repeat unit A. The two remaining signals are due to the other protons α to nitrogen in A.

D. Potential Applications

A characteristic common to the three classes of copolymers discussed in this dissertation is the high polarity of the copolymer backbone. While the resultant interchain attraction can cause solubility problems, it can also serve a useful purpose in each case. Further developmental work will be necessary, however, before the copolymers can be exploited.

The major drawback of the 1,4-dipole copolymers is their low molecular weight. If methods can be devised to raise the molecular weight, then it is possible that they could be structurally useful. The 1,4-intramolecular rearrangement also could be structurally useful as well as thermally stable if the problem of insolubility can be overcome.

The rapid, room temperature gelling of the Diels-Alder ene copolymer solutions may have application, such as a convenient method of suspending homoneneous solutions. The major drawback here lies in the exothermicity of the reaction. A large amount of heat is released, and scale up of this reaction could lead to difficult problems.

CHAPTER III

Experimental

A. General Information

Infrared spectra were taken on a Beckman IR-8 spectrophotometer and proton nuclear magnetic spectra on a Varian A-60A spectrometer except as noted. Mass spectral data were obtained using a Hitachi Perkin-Elmer RMU mass spectrometer. All ultraviolet and visible spectra were measured with a Beckman DK-2A spectrometer equipped with a Beckman 92529 Temperature Regulated Cell Holder for variable temperature work. Number average molecular weights were measured with a Mechrolab Model 302 Vapor Pressure Osmometer, and intrinsic viscosities were obtained by standard procedure using a Cannon-Ubbelohde semimicro dilution viscometer.

Melting points were taken on a Thomas-Hoover melting point apparatus and are reported in degrees centigrade uncorrected. Boiling points are also uncorrected and reported in degrees centigrade.

Elemental analyses were completed by either Atlantic Microlab, Inc., Atlanta, Georgia or Peninsular ChemResearch, Inc., Gainesville, Florida.

All reagents used in monomer synthesis, copolymerizations, and model compound studies were obtained commercially and used as received except as noted. All solvents were commercial grade and used as received with the exception of the solvents used in the visible absorption studies, which were spectral grade.

B. Synthesis of 4-Phenyl-1,2,4-Triazoline-3,5-dione

Ethyl carbazate[4]

Diethyl carbonate (1.80 mol., 200.0 g.) and 99% hydrazine hydrate (1.80 mol., 88.0 g.) were stirred at room temperature for one half hour. Initially the two phase system reacted with mild exothermicity, and one phase resulted. The clear liquid was distilled twice at 95° and 12 mm. yielding 130 g. (74.2%) of a liquid which on standing solidified to a white solid, m.p. 45-47° (lit.[4] 44-45.5°).

1-Ethoxycarbonyl-4-phenylsemicarbizide[74]

Ethyl carbazate (0.64 mol., 62.0 g.) was dissolved in 200 ml. benzene and was brought to 10° in a three-necked round bottomed flask equipped with an addition funnel, a reflux condenser fitted with a drying tube, a thermometer and a mechanical stirrer. Stirring was initiated and phenyl isocyanate (0.64 mol., 59.0 g.) in 100 ml. benzene was added dropwise through the addition funnel keeping the temperature between 10° and 20°. As the addition proceeded, a white precipitate appeared and remained until the addition was complete. The mixture was refluxed for one half hour, resulting in solution of the precipitate. Upon cooling the precipitate reappeared and was filtered. The precipitate was washed with two 75 ml. portions of cold benzene yielding 110.2 g. (91.3%) of a white solid, m.p. 151-52° (lit.[74] 154°).

4-Phenyl urazole[74]

1-Ethoxycarbonyl-4-phenylsemicarbazide (0.55 mol., 124.0 g.) was added to 300 ml. hot, stirred 4M potassium hydroxide. Upon complete solution, the light yellow solution was filtered and cooled. The solution was acidified with 50% hydrochloric acid resulting in a

voluminous white precipitate. The precipitate was vacuum filtered and washed several times with cold water. The filtrate was tested for additional precipitate by slowly adding 50% hydrochloric acid. Any solid that appeared was filtered, washed and combined with the original precipitate. The precipitate was dried overnight in a vacuum oven yielding 69 g. (78.1%) of a white solid, m.p. 204-208° (lit.[74] 206-7°).

4-Phenyl-1,2,4-triazoline-3,5-dione[8]

4-Phenyl urazole (3.43×10^{-2} mol., 6.0 g.) was placed in a 500 ml. Erlenmeyer flask containing 25 g. sodium sulfate; the mixture was cooled below 5° and a nitrogen sweep was placed above the solution level. Magnetic stirring was employed, and dinitrogen tetroxide gas was bubbled into the solution with stirring for one half hour. Nitrogen was passed into the solution to remove excess dinitrogen tetroxide gas, and then the solution was allowed to warm to room temperature. The solvent employed in the reaction, 300 ml. of methylene chloride, was removed by a rotory evaporator, and the solid was removed from the flask and allowed to air dry for two hours. The bright red solid was sublimed at 0.03 mm. and 70° yielding 5.3 g. (90.6%) of a red, crystalline solid. The material was stored in the freezer when not in use.

C. The 1,4-Dipole Copolymerizations

Reaction of PhTAD and 1,2-Dimethoxyethylene

1,2-Dimethoxyethylene (0.00286 mol., 0.252 g.) (80% trans) was dissolved in 20 ml. methylene chloride and added to a 20 ml. solution of PhTAD (0.00286 mol., 0.500 g.) in a 125 ml. Erlenmeyer flask. The addition caused the solvent to boil, and the characteristic red color of PhTAD disappeared immediately. The light yellow solution was allowed to stir an additional 15 minutes, and was then slowly added to 500 ml. of stirred hexane. The resulting precipitate was filtered, reprecipitated twice and dried, yielding 0.62 g. (80%) of a white solid. Analysis identified the amorphous solid as a copolymer having repeat units 42 and 43, softening at 160-170°. The nuclear magnetic resonance spectrum ($CDCl_3$) gave signals at δ3.3 (s, broad, 3), δ3.6 (s, broad, 3), δ5.3 (m, broad, 1), δ6.08 (m, broad, 1), and δ7.5 (s, broad, 5). Infrared absorbances were found at (KBr) 2960 (w), 2860 (w), 1780 (m), 1730 (s, b), 1610 (s), 1500 (m), 1470 (m), 1440 (m), 1330 (w), 1310 (w), 1200 (m), 1110 (w), 1060 (w), 1020 (w), 950 (w, b), 750 (w, b), and 690 (w) $cm.^{-1}$. Vapor pressure osmometry in acetone gave a number average molecular weight of 1860.

Anal. Calcd. for 1:1 copolymer, $C_{12}H_{13}N_3O_4$: C, 54.75; H, 4.98; N, 15.96. Found: C, 54.59; H, 5.08; N, 16.06.

The filtrate of the first precipitation was evaporated on a rotary evaporator yielding 0.090 g. (12%) of a light yellow solid. The solid, which by nuclear magnetic resonance analysis was shown to contain a small percentage of copolymer, was determined to be the corresponding 1,2-diazetidine. Resonance signals were found at ($CDCl_3$) δ3.30 (s),

δ3.61 (s), δ5.43 (d), δ6.91 (d), and δ7.50 (s). Attempted integration of the signals was not successful since the sample contained copolymer. The sample was heated in tetrahydrofuran for 12 hours, followed by precipitation as before. Nuclear magnetic resonance analysis gave resonance signals identical to those for the copolymer containing repeat units 42 and 43.

Reaction of PhTAD and p-2-vinyloxyethoxytoluene

p-2-Vinyloxyethoxytoluene (0.00286 mol., 0.510 g.) was dissolved in 15 ml. methylene chloride and was slowly added to a 20 ml. solution of PhTAD (0.00286 mol., 0.500 g.) in methylene chloride. In less than two minutes the red color changed to light pink, and a white precipitate formed in the 125 ml. Erlenmeyer flask. The color was completely discharged in ten minutes. The solid was filtered and washed twice yielding 0.493 g. (50%) of a white crystalline solid melting at 131-132°. Analysis indicated the solid to be a copolymer structured mostly as 44. Vapor pressure osmometry in acetone demonstrated the number average molecular weight to be 1430. Resonance signals in the nuclear magnetic resonance spectrum were found at ($CDCl_3$) δ2.2 (s, broad, 3), δ4.0 (m, very broad, 4), δ6.7 (m, broad, 3), and δ7.4 (s, broad, 4). Infrared absorbances were located at (KBr) 3060 (w), 2960 (w), 1780 (m), 1730 (s), 1710 (s), 1500 (m), 1420 (m), 1360 (w), 1300 (w), 1260 (m), 1250 (m), 1170 (w), 1130 (m), 1100 (w), 1080 (w), 1020 (w), 920 (w), 870 (w), 820 (w), 800 (w), 770 (w), 740 (w), 680 (w), and 670 (w) $cm.^{-1}$.

Anal. Calcd. for a 1:1 copolymer, $C_{19}H_{19}N_3O_4$: C, 64.58; H, 5.42; N, 11.79. Found: C, 64.66; H, 5.37; N, 11.79.

The filtrate of the reaction volume was slowly added to 500 ml. of stirred hexane resulting in an additional 0.347 g. of 44. Structural assignment was based upon its melting point of 129-132° and its nuclear magnetic resonance spectrum, which had signals identical to those of the first precipitate. The total yield of copolymer in the reaction was 0.840 g. (83%).

Reaction of PhTAD and 1-vinyl-2-pyrrolidone

1-Vinyl-2-pyrrolidone (0.00286 mol., 0.308 g.) was dissolved in 35 ml. methylene chloride and added to a solution of PhTAD (0.00286 mol., 0.500 g.) in 20 ml. methylene chloride. The resultant solution began to boil in the 125 ml. Erlenmeyer flask, and the red color discharged in less than thirty seconds. The light yellow solution was slowly added to 500 ml. of stirred hexane as before, precipitating 0.714 g. (88%) of a white solid which softened in the range of 175-185°. Nuclear magnetic resonance and infrared spectral analysis indicated the amorphous solid to be the copolymer, 45. The nuclear magnetic resonance spectrum gave resonance signals at ($CDCl_3$) δ2.2 (m, very broad, 6), δ3.6 (m, very broad, 2), δ6.1 (m, very broad), and δ7.4 (s, broad, 5). Infrared absorbances were found at (KBr) 3080 (w), 2980 (w), 1780 (m), 1720 (s, b), 1610 (w), 1500 (m), 1420 (s), 1320 (w), 1280 (m), 1270 (m), 1230 (w), 1160 (w), 1070 (w), 1030 (w), 770 (m), 690 (w), and 630 (w) $cm.^{-1}$. The number average molecular weight was determined to be 1100 by vapor pressure osmometry using acetone as the solvent.

Anal. Calcd. for a 1:1 copolymer, $C_{14}H_{14}N_4O_3$: C, 58.75; H, 4.93; N, 19.58. Found: C, 57.05; H, 5.14; N, 18.98.

Reaction of PhTAD and N-vinylsuccinimide

N-Vinylsuccinimide (0.00286 mol., 0.358 g.) was dissolved in 30 ml. of methylene chloride and added to a 20 ml. solution of PhTAD in a 125 ml. Erlenmeyer flask. The color rapidly disappeared giving rise to a light yellow solution. The solution was slowly added to 500 ml. of hexane yielding a light yellow solid. The solid was filtered and reprecipitated twice yielding 0.725 g. (85%) of a light yellow solid. Analysis as before identified the amorphous solid to be the copolymer, 46. The solid softened in the 150-160° range. The number average molecular weight was determined to be 1400 by vapor pressure osmometry in acetone. Nuclear magnetic resonance signals for 46 were found at ($CDCl_3$) δ2.6 (m, very broad, 4), δ4.5 (m, very broad, 3), and δ7.5 (s, broad, 5). Infrared absorbances appeared at (KBr) 3060 (w), 2980 (w), 1780 (m), 1720 (s), 1705 (s), 1610 (w), 1500 (w), 1410 (s), 1320 (w), 1280 (m), 1270 (m), 1200 (w), 1160 (w), 1070 (w), 1030 (w), 770 (m), 650 (w), and 620 (w) $cm.^{-1}$.

Anal. Calcd. for a 1:1 copolymer, $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.74; H, 4.19; N, 18.66.

General procedure for copolymer separation in the reactions of PhTAD and vinyl esters

The general reaction procedure for the PhTAD and vinyl ester reactions is described in section "D" of this chapter. The copolymer that precipitated in hexane was redissolved in hot hexane and reprecipitated twice and dried at 58°/0.03 mm. before analysis. Specific information concerning these copolymers is given below.

Copolymer of PhTAD and vinyl benzoate

A white, amorphous solid weighing 0.791 g. (87%) was obtained softening in the 150-165° range. Vapor pressure osmometry analysis in acetone indicated the number average molecular weight to be 1200. Resonance signals ($CDCl_3$) in the nuclear magnetic resonance spectra were found at δ4.5 (s, broad), δ7.45 (m, very broad), and δ7.8 (s, broad). Integration of the spectrum and elemental analysis indicated that the copolymer did not exist in a 1:1 ratio of comonomers. Infrared absorbances were located at (KBr) 3080 (w), 1780 (m), 1735 (s,b), 1615 (m), 1600 (m), 1500 (m), 1420 (m), 1320 (m), 1250 (m), 1110 (w), 1060 (w), 1020 (w), 810 (m), and 690 (m) $cm.^{-1}$.

Anal. Calcd. for a 1:1 copolymer, $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 61.10; H, 4.19; N, 14.92. The molar ratio (PhTAD/vinyl benzoate) in the copolymer was 1.27/1.

Reaction of PhTAD and vinyl benzoate using a 10:1 monomer ratio of PhTAD to vinyl benzoate

Vinyl benzoate (0.00143 mol., 0.162 g.) was dissolved in 20 ml. methylene chloride, and this solution was mixed with a 30 ml. solution of PhTAD (0.0143 mol., 2.500 g.). The red solution was divided into two equal portions, one for a study of the reaction at room temperature, and the other for an examination of the reaction at 60°. The solution was studied at 60° and sealed in a glass tube as described in section "D" of this chapter. The reactions were allowed to continue for six hours, after which the red solutions were filtered to remove a small amount of insoluble solid and poured into 250 ml. portions of stirred hexane. The resulting copolymers were washed several times with cold

hexane and reprecipitated into hot hexane twice. The solids were then dried at 58°/0.03 mm. overnight and submitted for analysis. The results are given below.

Anal. for copolymer of room temperature reaction. Calcd. for a 1:1 copolymer, $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 58.09; H, 4.05; N, 17.97. The molar ratio (PhTAD/vinyl benzoate) in the copolymer was 2.37/1.

Anal. for copolymer of 60° reaction. Calcd. for a 1:1 copolymer, $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 57.08; H, 3.82; N, 18.55. The molar ratio (PhTAD/vinyl benzoate) in the copolymer was 2.82/1.

Copolymer of PhTAD and vinyl isobutyrate

A white, amorphous solid weighing 0.123 g. (12%) and softening at 140-150° resulted from the purification procedure. Vapor pressure osmometry analysis in acetone gave a number average molecular weight of 1250. Nuclear magnetic resonance signals were observed at δ1.3 (very broad), δ3.6 (very broad, almost indistinguishable), δ4.3 (very broad), and δ7.4 (s, broad). Elemental analysis and the nuclear magnetic resonance integration showed that the copolymer did not exist in a 1:1 ratio of comonomers. Infrared absorbances were found at (KBr) 2980 (w), 1780 (m), 1735 (s, b), 1610 (m), 1600 (m), 1420 (m), 1250 (m), 1140 (w), 1060 (w), 1020 (w), 960 (m), 750 (m), and 690 (m) $cm.^{-1}$.

Anal. Calcd. for a 1:1 copolymer, $C_{14}H_9N_3O_4$: C, 58.13; H, 5.23; N, 14.53. Found: C, 56.78; H, 4.68; N, 17.65. The molar ratio (PhTAD/vinyl isobutyrate) in the copolymer was 1.32/1.

Copolymer of PhTAD and vinyl pivalate

As before, a white, amorphous solid resulted from the purification procedure weighing 0.133 g. (16%). The solid melted in a range of 165-170°, and vapor pressure osmometry in acetone gave a number average molecular weight of 1300. Other samples prepared gave number average molecular weights in the range of 1230 to 1500. The nuclear magnetic resonance spectrum ($CDCl_3$) gave signals at δ1.1 (s, broad, δ4.2 (very broad), and δ7.5 (s, broad). As with the other PhTAD/vinyl ester copolymers, the elemental analysis and the nuclear magnetic resonance integration demonstrated that the copolymer did not exist in a 1:1 ratio of comonomers. Absorbances in the infrared spectrum were found at (KBr) 3080 (w), 1780 (m), 1730 (s, b), 1610 (m), 1600 (m), 1500 (m), 1450 (m), 1420 (m), 1310 (m), 1250 (m), 1180 (w), 1060 (m), 1020 (w), 760 (m), 710 (m), and 690 (m) $cm.^{-1}$.

Anal. Calcd. for a 1:1 copolymer, $C_{15}H_{17}N_3O_4$: C, 57.40; H, 5.65; N, 13.85. Found: C, 57.59; H, 5.25; N, 16.71. The molar ratio (PhTAD/vinyl pivalate) in the copolymer was 1.72/1.

Another sample of the PhTAD/vinyl pivalate copolymer, prepared by the same procedure, was submitted for elemental analysis, and the results, shown below, compared favorably with those of the first analysis.

Anal. Calcd. for a 1:1 copolymer, $C_{15}H_{17}N_3O_4$: C, 57.40; H, 5.65; N, 13.85. Found: C, 57.48; H, 4.91; N, 16.56. The molar ratio (PhTAD/vinyl pivalate) in the copolymer was 1.69/1.

Nuclear magnetic resonance analysis of the PhTAD/ethyl vinyl ether reaction at low temperatures

A 100 ml. solution of ethyl vinyl ether (5.71×10^{-5} mol., 0.0094 g.) was prepared by diluting 1 ml. of a 5.71×10^{-3} molar solution to 100 ml. A 100 ml. solution of PhTAD (5.71×10^{-5} mol., 0.0099 g.) was prepared in an identical manner. The two solutions were cooled to -10° in a dry ice/isopropanol bath and were then mixed together, discharging the red color of PhTAD instantaneously. A nuclear magnetic resonance tube was also cooled to -10°, and a sample of the above solution was introduced into the tube. The tube was placed in the sample chamber of the spectrometer, which had been regulated to -9°, and a nuclear magnetic resonance spectrum was made immediately. Some copolymer was present, as noted by its characteristically broad signals, but the major signals of the spectrum were those of the 1,2-diazetidine located at δ1.48 (t), δ4.1 (m), δ4.65 (m), δ5.80 (t), and δ7.65 (s). The solution was warmed to +2°, and continuous sweeps were made over a 30-minute period. During that time, the signals at δ4.65 and δ5.80 disappeared while a very broad signal at δ4.0 appeared coalescing with the original signal at δ4.1. The other signals at δ1.48 and at δ7.65 also broadened considerably.

D. The 1,4-Dipole Intramolecular Rearrangement

General procedure

To a solution of 0.500 g. (2.86×10^{-3} mol.) of PhTAD in 25 ml. of methylene chloride (dried over 4-Å molecular sieves) was added a 25 ml. solution of 2.86×10^{-3} mol. of the vinyl ester. The intense red solution was transferred to a thick-walled glass tube, which was sealed under vacuum following two freeze-thaw cycles in liquid nitrogen. The tube was placed in a 60° constant-temperature bath and removed after color discharge to light yellow was noted. The tube was then opened and the contents were poured through a coarse sintered glass funnel into 250 ml. of stirred hexane to precipitate any copolymer formed. Copolymer, if present, was filtered and the filtrate was evaporated on a rotary evaporator, leaving a residue of nonpolymeric products. The nonpolymeric products were separated and purified as described below, and dried at 58° (0.03 mm.) overnight before analysis. All nonpolymeric products were odorless, white, crystalline solids; the copolymers were odorless, white amorphous solids. Nuclear magnetic resonance data may be found in Table V. Analysis of the copolymers is described in section "C" of this chapter.

1-Acetylmethyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione

1-Acetylmethyl-2-acetyl-phenyl-1,2,4-triazoline-3,5-dione, 53, was recrystallized twice from a methylene chloride-hexane solvent pair yielding 0.56 g. (75%) of product, m.p. 130-131°. Infrared absorbances were located at (KBr) 3080 (w), 3020 (w), 2980 (w), 2960 (w), 1800 (s), 1750 (s), 1730 (s), 1720 (w), 1590 (w), 1500 (m), 1460 (m, sh), 1415 (s), 1365 (m), 1320 (m), 1260 (s), 1240 (s), 1170 (s), 1135 (m),

1080 (w), 1030 (w), 990 (w), 930 (w), 830 (w), 760 (m), 720 (w), 680 (w), 640 (w), and 620 (w) cm.$^{-1}$. The molecular ion was found at 275 m/e in the mass spectrum.

Anal. Calcd. for $C_{13}H_{12}N_3O_4$: C, 56.73; H, 4.75; N, 15.27. Found: C, 56.83; H, 4.80; N, 15.33.

1-Formylmethyl-2-chloroacetyl-4-phenyl-1,2,4-triazoline-3,5-dione, 55, precipitated upon pouring the reaction mixture into 250 ml. of stirred hexane. Nuclear magnetic resonance analysis of the crude material indicated no copolymer formation. Purification was effected by twice recrystallizing the crude product from hexane-methylene chloride yielding 0.80 g. (95%) of product, m.p. 157-158°. The infrared spectrum exhibited absorbances at (KBr) 3030 (w), 3010 (w), 2990 (w), 2880 (w), 2745 (w), 1810 (s), 1760-1710 (s, b), 1600 (w), 1510 (s), 1430 (s), 1400 (m), 1330 (m), 1330 (m), 1310 (w), 1240 (m), 1210 (m), 1190 (m), 1120 (m), 1090 (m), 1070 (m), 1020 (m), 960 (w), 920 (w), 880 (w), 860 (w), 820 (w), 780 (m)- 760 (m), 740 (m), 700 (s), 650 (m), and 620 (m). The molecular ion was located at 295 m/e in the mass spectrum.

Anal. Calcd. for $C_{12}H_{10}ClN_3O_4$: C, 48.91; H, 3.42; N, 14.26. Found: C, 49.00; H, 3.58; N, 14.20.

1-Formylmethyl-2-benzoyloxy-4-phenyl-1,2,4-triazoline-3,5-dione, 57, and 3-phenyl-6-benzoyloxy-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione, 58, could not be separated by fractional crystallization or column chromatography using alumina and methylene chloride as the eluent. Their structural assignments were made based upon the nuclear magnetic resonance spectrum of the mixture, total yield 0.11 g. (13%).

1-Formylmethyl-2-(2-methylpropionyl)-4-phenyl-1,2,4-triazoline-3,5-dione, 60, and 3-phenyl-6-(2-methylpropionyloxy)-1,3,5-triaza-

bicyclo[3.2.0]hepta-2,4-dione, 61, appeared as an oil after evaporation of the solvent. The mixture was dissolved in the minimum amount of methylene chloride necessary to attain solution followed by addition of the minimum amount of hexane to cause cloudiness. The solution was allowed to stand at room temperature for two to three days, resulting in fractional crystallization (61 crystallized first) of the solids. The procedure was repeated several times in order to obtain a pure sample of 60. The data for 60 are as follows: yield 0.50 g. (60%); m.p. 100-101°; infrared (KBr) 3040 (w), 3000 (w), 3870 (w), 2750 (w), 1800 (s), 1735 (s, b), 1720 (s, sh), 1600 (w), 1500 (m), 1460 (s), 1420 (s), 1380 (m), 1350 (m), 1260 (m), 1200 (m), 1180 (m), 1100 (m), 1080 (w), 1020 (w), 950 (w), 890 (w), 860 (w), 840 (w), 790 (w), 750 (w), 740 (w), 690 (w), 640 (w), and 620 (w) $cm.^{-1}$; molecular ion at 289 m/e; anal. calcd. for $C_{15}H_{15}N_3O_4$: C, 58.13; H, 5.23; N, 14.53. Found: C, 58.29; H, 5.36; N, 14.45. The data for 61 are as follows: yield 0.50 g. (6.3%); m.p. 163-164°; infrared (KBr) 3049 (w), 3040 (w), 2990 (w), 2940 (w), 2890 (w), 1780 (m), 1755 (s), 1720 (s), 1600 (w), 1500 (m), 1460 (m), 1410 (s), 1380 (m), 1360 (m), 1340 (m), 1295 (w), 1265 (m), 1240 (m), 1190 (m), 1140 (s), 1110 (m), 1060 (m), 1020 (m), 960 (w), 920 (w), 870 (w), 840 (w), 810 (w), 770 (m), 740 (m), 690 (m), 670 (w), and 620 (w) $cm.^{-1}$; molecular ion at 289 m/e; anal. calcd. for $C_{14}H_{15}N_3O_4$: C, 58.13; H, 5.23; N, 14.53. Found: C, 58.00; H, 5.31; N, 14.36.

1-Formylmethyl-2-(2,2-dimethylpropionyl)-4-phenyl-1,2,4-triazoline-3,5-dione, 63, and 3-phenyl-6-(2,2-dimethylpropionyl)-1,3,5-triaza-bicyclo[3.2.0]hepta-2,4-dione, 64, were purified using the same procedure employed for 60 and 61, substituting hexane-ether as the solvent

pair. The data for 63 are as follows: yield 0.31 g. (36%); m.p. 135-136°; infrared (KBr) 2990 (w), 2880 (w), 2740 (w), 1780 (m), 1740 (s), 1720 (s), 1700 (s), 1600 (w), 1500 (m), 1420 (s), 1400 (m), 1370 (m), 1330 (m), 1270 (m), 1220 (m), 1180 (m), 1110 (m), 1090 (w), 1070 (w), 1010 (w), 940 (w), 870 (w), 840 (w), 820 (w), 770 (w), 760 (w), 730 (w), 690 (w), and 640 (w); molecular ion at 303 m/e; anal. calcd. for $C_{15}H_{17}N_3O_4$: C, 59.40; H, 5.65; N, 13.85. Found: C, 59.30; H, 5.79; N, 13.79. The data for 64 are as follows: yield 0.31 g. (36%0; m.p. 171-172°; infrared (KBr) 3100 (w), 2990 (w), 2900 (w), 1780 (m), 1750 (s), 1725 (s), 1600 (w), 1500 (m), 1480 (w), 1460 (w), 1410 (m), 1360 (w), 1290 (w), 1280 (w), 1250 (w), 1130 (m), 1080 (w), 1050 (w), 1030 (w), 870 (w), 770 (w), 740 (w), 690 (w), and 640 (w) $cm.^{-1}$; molecular ion at 303 m/e; anal. calcd. for $C_{15}H_{17}N_3O_4$: C, 59.40; H, 5.65; N, 13.85. Found: C, 59.18; H, 5.70; N, 13.89.

Attempted reaction of vinyl trifluoroacetate

Vinyl trifluoroacetate was allowed to stand with PhTAD for 96 hours at 60°. Approximately 80% of PhTAD was recovered unreacted along with 10% of a tan solid, which appeared to be an oligomeric decomposition product of PhTAD by comparison of its infrared spectrum with the spectrum of a known sample.[61]

Procedure for kinetic measurements

One ml. portions of equimolar solutions of vinyl ester and PhTAD in 1,1,2,2-tetrachloroethane were pipetted into a pressure resistant ultraviolet cell. Visible spectra were recorded and the PhTAD absorbance at 545 nanometers was measured versus time. A minimum of seven readings were taken during each run. The reaction was determined to be second

order overall by fitting the data in the second order rate expression (equation 4), which assumes formation of the 1,4-dipole to be irreversible. The reaction was determined to be first order in each reactant

equation 4 $\frac{1}{A_t} = \frac{k}{a}t + \frac{1}{A_o}$

A_t=absorbance, time t
a=PhTAD absorptivity coefficient X cell path length
k=second order rate constant
A_o=initial absorbance

by noting a ten fold increase in rate when using a ten to one molar ratio of vinyl ester to PhTAD, indicating the reaction to be first order in vinyl ester. The results were double checked by fitting the ten to one molar ratio data in the first order rate expression (equation 5) demonstrating the reaction to be pseudo first order in PhTAD under these conditions. Energies of activation, calculated by

equation 5 $\ln \frac{A_t}{a} = kt + A_o$ k = first order rate constant

the Arrhenius method, are listed to three significant figures in Table X. Second order rate constants measured at temperatures other than 60° are reported also. Entropies of activation were calculated by use of equation 3 (described in section "B", Chapter II).

Procedure used for checking thermal stability of 64

A sample of the solid resulting from reaction of PhTAD and vinyl pivalate was dissolved in chloroform-d_1 and its nuclear magnetic resonance spectrum taken. The spectrum sppeared as a superimposition of the spectra of the three pure products. Of special note was the ratio (1.2:1.0) of the t-butyl singlets of the monomeric products, one at δ1.37 corresponding to the t-butyl group of 63, the other at δ1.20

Table X

Kinetic Data for the Vinyl Ester/PhTAD Reactions[a]

Measured at Various Temperatures

Vinyl Ester	Temp., °C	k, ℓ/mol-sec(C of C)[b]	ΔE_{act}, Kcal/mol
Isopropenyl Acetate	34.8	1.0×10^{-1}	7.44
	40.6	1.5×10^{-1}	
	48.1	2.0×10^{-1}	
Vinyl Acetate	44.5	1.7×10^{-2} (0.998)	11.9
	68.3	6.1×10^{-2}	
	74.9	9.1×10^{-2}	
Vinyl Isobutyrate	69.7	9.9×10^{-2}	11.6
	78.8	1.8×10^{-1}	
	90.0	2.5×10^{-1} (0.998)	
Vinyl Pivalate	51.1	2.6×10^{-2}	12.1
	73.1	8.5×10^{-2}	
	80.2	1.2×10^{-1}	
Vinyl Chloroacetate	71.3	1.8×10^{-2}	13.6
	78.3	2.7×10^{-2}	
	90.0	5.0×10^{-2}	
	101.5	9.0×10^{-2}	
Vinyl Benzoate	62.5	3.8×10^{-2}	10.7
	69.0	5.7×10^{-2}	
	75.7	7.2×10^{-2}	
	80.0	8.4×10^{-2}	

[a] Since the third decimal place in the absorbance readings was estimated, these values are accurate to two decimal places only, as reported in Table I.

[b] Coefficient of correlation, as in Table VII.

caused by the t-butyl group of 64. The nuclear magnetic resonance tube was heated at 60° for sixteen hours followed by spectral analysis. No change in the t-butyl ratio occurred, and there was no noticeable increase in copolymer; thus, it was concluded that the 1,2-diazetidine, 64, did not ring open.

Reaction of 1-formyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione, 34 and ethanol - acetal formation

1-Formyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione, 34, (0.00383 mol., 1.000 g.) was added to 50.0 ml. absolute ethanol in a 100 ml. round bottomed flask. A small crystal of toluenesulfonic acid was added along with 30.0 g. of anhydrous Na_2SO_4, and the mixture was refluxed for one half hour. The solution was allowed to stand overnight, after which the solid Na_2SO_4 was filtered and the filtrate evaporated yielding a light yellow oil (0.988 g., 91%), identified by nuclear magnetic resonance as 1-(1,1-ethoxy-2-ethyl)-2-hydro-4-phenyl-1,2,4-triazoline-3,5-dione. Apparently the acetoxy group at the "2" position was cleaved under the reaction conditions. Nuclear magnetic resonance signals were found at ($CDCl_3$) δ1.21 (t, 6), δ3.65 (m, 6), δ4.80 (t, 1), δ6.64 (broad singlet, 1 (N-H proton)), and δ7.48 (s, 5). The attempted vacuum distillation of the light yellow oil to obtain an analytically pure sample resulted in decomposition of the acetal.

E. Bis-Triazoline-dione Copolymerizations

Synthesis of bis-(p-3,5-dioxo-1,2,4-triazolin-4-ylphenyl)methane, 69[52]

A 100 ml. solution of bis-(4-isocyanatophenyl)methane (0.100 mol., 24.0 g.), vacuum distilled before use, was slowly added to a 200 ml. solution of ethyl carbazate (0.200 mol., 19.0 g.) in benzene, which was cooled to maintain the temperature at 45° or below. After the addition was complete, the mechanically stirred mixture was refluxed for one half hour to insure complete reaction. The resulting insoluble, white solid was filtered, and dried after stirring overnight. The bis-semi-carbazide, 67, melted at 236-245° (lit.[52] 240-244°) and weighed 40.1 g. (93%).

The bis-semicarbazide (0.087 mol., 40.0 g.) was slowly added to a 100 ml. 4N aqueous solution of potassium hydroxide and 100 ml. ethanol. The mixture was heated on a steam bath for two hours followed by filtration of a small amount of insoluble solid. The light yellow filtrate was slowly added to an excess of 5% aqueous acetic acid, precipitating the bis-urazole, 68, an off-white solid, m.p. 325° (decomposition), (lit.[52] 320°). The yield was 34.9 g. (95%).

The bis-urazole (0.095 mol., 34.9 g.) was suspended in 50 ml. methylene chloride by magnetic stirring and cooled to -10°, followed by the addition of 1.0 ml. of fuming nitric acid over a 10 minute period. A red color was immediately generated during the addition, and the solution was allowed to stir for 5 minutes after the addition. The solution was washed with 200 ml. cold water, dried cold over sodium sulfate, and evaporated to dryness at reduced pressure (5-10 mm.) below room temperature. The red solid that resulted was dissolved

in 15 ml. ethyl acetate, filtered, and slowly added to 150 ml. low boiling petroleum ether causing precipitation of the bis-triazoline-dione, 69. The procedure was repeated twice to insure purification yielding 16.9 g. (70%) of product. The red solid did not melt, but changed color to tan at 335° (lit.[52] 320°).

Anal. Calcd. for $C_{17}H_{10}N_6O_4$: C, 56.36; H, 2.98; N, 23.20. Found: C, 56.47; H, 2.90; N, 22.63.

Synthesis of 1,6-hexane-bis-1,2,4-triazoline-3,5-dione, 73

Freshly distilled 1,6-hexanediisocyanate (0.238 mol., 40.0 g.) was dissolved in 10 ml. benzene. This solution was dropped slowly into a solution of ethyl carbazate (0.476 mol., 49.5 g.) in 200 ml. benzene. The diisocyanate was added at room temperature, and the rate of addition was controlled to maintain the temperature at 30° or below. After the addition was complete, the voluminous white slurry was stirred at room temperature for one half hour, then refluxed gently for two hours. The bis-semicarbazide, 70, was removed by vacuum filtration and then dried under vacuum at 50° overnight, yielding 88.0 g. (98%) of product, m.p. 201-203°. Infrared absorbances were observed at (KBr) 3380 (s), 3305 (s, b), 1735 (s), 1685 (s), 1450 (m), 1400 (m), 1370 (w), 1310 (m), 1225 (s), 1110 (w), 1095 (w), 900 (w), 850 (w), 760 (m), and 615 (m) $cm.^{-1}$. Nuclear magnetic resonance signals were found at (DMSO-d_6) δ1.06 (t, 6, J 7 Hz.), δ1.17 (m, 8), δ2.87 (m, 4), δ3.92 (q, 4, J 7 Hz.), δ6.10 (distorted triplet, 2), δ7.50 (broad singlet, 2), and δ8.40 (broad singlet, 2).

Anal. Calcd. for $C_{14}H_{28}N_6O_6$: C, 44.67; H, 7.50; N, 22.33. Found: C, 44.82; H, 7.60; N, 22.39.

Sodium hydride (1.59 mol. equiv. Na, 7.65 g. of 50% oil dispersion), was slowly added to 750 ml. absolute ethanol. After complete evolution of hydrogen, the solution was filtered and poured over the bis-semicarbazide, 70, (0.0797 mol., 30.0 g.) in a 1-liter 3-necked found bottomed flask. The slurry was stirred mechanically and refluxed for 24 hours. A light brown solid, 16.7 g. (75%) was filtered and dried overnight under vacuum at 150°. A portion of this solid (m.p. 310°) was dissolved in water and neutralized with 50% HCl until a pH of 7 was attained. The clear solution was placed in a freezer at -10° resulting in low yield precipitation of 1,6-hexane-diurazole, 72. The offwhite solid melted in a range of 211-216°. Infrared absorbances were found at (KBr) 3700-3100 (m, very broad), 3310 (m, shoulder), 2950 (w), 1690 (s, b), 1470 (m), 1430 (w), 1360 (w), 1330 (w), 1180 (w), 1080 (w), 970 (w), 850 (w), 790 (m), 720 (w), and 640 (w) $cm.^{-1}$. Nuclear magnetic resonance signals were observed at (DMSO-d_6) δ1.48 (m, 8), δ3.48 (distorted triplet, 4), and δ10.07 (broad, 4).

Anal. Calcd. for $C_{10}H_{14}N_6O_4$: C, 42.25; H, 5.67; N, 29.56. Found: C, 42.25; H, 5.86; N, 29.33.

Sodium sulfate (anhydrous, 25.0 g.) was added to 300 ml. methylene chloride, and the magnetically stirred slurry was cooled to 5°. The diurazole, 72, (or the light brown solid, presumably the diurazole salt) (0.0176 mol., 5.00 g.) was added and dinitrogen tetroxide was bubbled slowly through the stirring slurry until a dark reddish-purple color persisted (about 30 minutes). The sodium sulfate was removed by filtration and the dard red filtrate was evaporated on a rotary evaporator using lukewarm water. A light pink solid remained as a residue, which was dissolved in 20 ml. of ethyl acetate. The red

solution was filtered, then slowly dropped into 200 ml. petroleum ether (b.p. 20-40°) resulting in the precipitation of a light pink solid weighing 3.4 g. (70%), identified by analysis to be the desired bis-triazoline-dione, 73. The product was dried in the dark overnight after filtration. The solid decomposed at 170-175°. Infrared absorbances were found at (KBr) 2920 (w), 1770 (m), 1735 (s, b), 1520 (w), 1430 (w), 1380 (m), 1340 (w), 1310 (w), 1240 (w), 1180 (w), 1110 (w), 710 (w), and 660 (m) $cm.^{-1}$. Nuclear magnetic resonance signals were observed at (DMSO-d_6) δ1.43 (m, 8) and δ3.43 (distorted triplet, 4).

Anal. Calcd. for $C_{10}H_{12}N_6O_4$: C, 42.86; H, 4.32; N, 29.99. Found: C, 42.58; H, 4.51; N, 29.83.

Attempted cyclization of 70 using potassium hydroxide

In an attempt to generate the diurazole, 72, by normal procedure, the bis-semicarbazide (0.106 mol., 40.0 g.) was slowly added to 250 ml. 4M solution of potassium hydroxide on a steam bath. The bis-semicarbazide went into solution as before, requiring more time, however. The solution was filtered hot, then diluted with an additional 200 ml. distilled water. The light yellow solution was neutralized with 50% HCl. When the pH approached 7, a gas began to evolve, and at a pH of 7, large amounts of the gas were produced upon addition of small quantities of acid. No precipitate appeared as had been observed in the synthesis of other urazoles. A sample of the gas was trapped, and its infrared spectrum measured; infrared absorbances were located at (gas cell) 3760 (w, sharp), 3740 (w, sharp), 2340 (s), 670 (m), and 650 (m, shoulder) $cm.^{-1}$. Since the gas was thought to be CO_2, a sample of CO_2 was generated by acidifying an aqueous solution of

$CaCO_3$. The infrared spectrum of this gas was identical to the gas evolved in the attempted cyclization reaction, with infrared absorbances being attributed to the presence of CO_2 and water vapor; thus, 71 was proposed as the product of the attempted cyclization rather than 72.

Efforts to effect the cyclization of 70 in alcoholic potassium hydroxide also led to the proposed structure 71, rather than the diurazole, 72.

Synthesis of 80, a model compound for the 1,4-dipole intramolecular rearrangement copolymerizations

1,6-Hexane-bis-1,2,4-triazoline-3,5-dione, 73, (0.00125 mol., 0.351 g.) was dissolved in 20 ml. tetrahydrofuran and was slowly added to a 20 ml. solution of isopropenyl acetate (0.00251 mol., 0.251 g.). The red solution was stirred magnetically at room temperature overnight. The following morning the solution was light yellow indicating that the reaction was complete. The solvent was evaporated, and the residue weighing 0.500 g. (83%) was dried at 58/0.03 mm. overnight. Nuclear magnetic resonance signals were found at (DMSO-d_6) δ1.43 (m, 8), δ2.13 (s, 6), δ2.53 (s, 6), δ3.62 (distorted triplet, 4, J=6 Hz.), and δ4.82 (s, 4), which was consistent with the assigned structure, 80.

Synthesis of 81, a model compound for the 1,4-dipole intramolecular rearrangement copolymerizations

4-Methyl-1,2,4-triazoline-3,5-dione, 84, (0.00254 mol., 0.287 g.) was dissolved in 20 ml. tetrahydrofuran and was slowly added to a

20 ml. solution of the diisopropenyl ester of adipic acid, 74 (0.00127 mol., 0.257 g.). The red solution was stirred magnetically overnight resulting in discharge of the red color to light yellow. The solvent was evaporated, and the residue weighing 0.490 g. (90%) was dried at 58°/0.03 mm. overnight. Nuclear magnetic resonance signals were observed at (DMSO-d_6) δ1.60 (m, 4), δ2.12 (s, 6), δ2.90 (m, 4), δ2.92 (s, 3), δ3.18 (s, 3), and δ4.72 (s, 4), which was consistent with the assigned structure, 81.

Synthesis of diisopropenyl adipate, 74[70]

To a one-necked three liter flask containing siopropenyl acetate (3.09 mol., 309.0 g.) was added adipic acid (0.772 mol., 113 g.). The flask was equipped with a mechanical stirrer, a thermometer, and a reflux condenser, and the stirred solution was heated to 96-99° for 48 hours. During this period a homogeneous yellow solution was attained. The solution was allowed to cool and was then washed with 100 ml. of a cold, saturated Na_2CO_3 solution to neutralize the acetic acid. The solution was washed with additional, smaller portions until no further CO_2 was released. The light yellow solution was then stored over 100 g. anhydrous Na_2SO_4 for four days. The solution was then vacuum distilled through a fractionating column collecting the fraction boiling between 95° and 105°/0.75 mm. The clear, colorless liquid was placed on an alumina column one inch in diameter and six inches long, and washed through with low boiling (20-40°) petroleum ether. Five 20 ml. samples were collected. The low boiling ether was evaporated on a rotary evaporator leaving a clear, colorless liquid, identified as the desired product, 74, behind. Nuclear

magnetic resonance signals were located at ($CDCl_3$) δ1.69 (m, 4), δ1.90 (s, 6), δ2.32 (m, 4), and δ4.61 (broad singlet, 4). The refractive index at 26° was 1.4481. The total yield for the reaction was 18.9 g. (12%).

Synthesis of divinyl adipate, 75[71]

Freshly distilled vinyl acetate (3.22 mol., 278.0 g.) was placed in a 500 ml. round bottomed 3 necked flask equipped with a reflux condenser, a mechanical stirrer and a thermometer. Adipic acid (0.204 mol., 30.0 g.) was then added along with 1.0 g. Hg $(OAc)_2$, 50 mg. Cu powder, and 0.2 ml. H_2SO_4. The mixture was refluxed for 12 hours. After this period, metallic mercury had appeared, and the solution had turned dark green. The solution was allowed to cool, and 0.8 g. NaAc was added. The mixture was transferred to a 500 ml round bottomed flask, and the excess vinyl acetate and acetic acid was removed on a rotary evaporator. The residual solution was transferred to a 100 ml. round bottomed flask, and the mixture was vacuum distilled through a fractionating column collecting the fraction boiling between 90° and 120°/2 mm. The clear, colorless liquid was redistilled on a spinning band distillation column, and the fraction boiling at 105-110°/2 mm. was collected and identified as the desired product, 75. The refractive index at 26° was 1.4515. Nuclear magnetic resonance signals were observed at ($CDCl_3$) δ1.65 (m, 4), δ2.39 (m, 4), δ4.7 (m, 4), and δ7.2 (4 signals, 2). Since the nuclear magnetic resonance spectrum was as described in the literature, no further purification was necessary. The total yield of the reaction was 27.9 g. (49%).

Attempted synthesis of diisopropenyl terephthalate

Terephthalic acid (0.772 mol., 128.0 g.) was added to diisopropenyl acetate (3.09 mol., 309.0 g.) in a 1 liter, 3-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. $Hg(OAc)_2$ (3.0 g.) was added to catalyze the reaction, and the heterogeneous mixture was maintained at 96-99° for 48 hours. No reaction occurred. After adding 20 drops of H_2SO_4, the mixture was once again refluxed at 96-99°. A very dark solution resulted after 48 hours, which solidified after cooling; apparently, the isopropenyl acetate homopolymerized as evidenced by the very broad signals in the nuclear magnetic resonance spectrum of the solid.

Dimethyl terephthalate (0.500 mol., 89.0 g.) was mixed with diisopropenyl acetate (3.09 mol., 309.0 g.) in a 1 liter, 3-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. A homogeneous solution resulted which was heated to 85° for 48 hours. During this time, the solution turned very dark yellow. In attempting to fractionate the solution under vacuum, the liquid became highly viscous after the excess isopropenyl acetate distilled, and no further liquid came over. No further purification was attempted.

Copolymerization of 73 and 74 at room temperature

Diisopropenyl adipate, 74, (0.002144 mol., 0.4335 g.) was dissolved in 15 ml. tetrahydrofuran, and was slowly added to a 20 ml. solution of the bis-triazoline-dione, 73 (0.002144 mol., 0.6007 g.). The solution was placed in a thick-walled glass tube, degassed by two liquid nitrogen freeze-thaw cycles, and sealed under vacuum. The red solution was allowed to stand overnight resulting in the discharge

of the red color and the formation of a light yellow gel. The gel was filtered and washed with cold solvent, followed by drying overnight at 58°/0.03 mm., giving a light yellow solid weighing 0.848 g. (82%). The solid was found to be insoluble in methylene chloride, chloroform, acetone, petroleum and ethyl ether, tetrahydrofuran, hexane, water, ethanol, methanol, ethyl acetate, nitromethane, benzene, hexamethylphosphoritriamide, and N-methylpyrrolidone. The solid was observed to swell considerably in dimethyl sulfoxide and dimethylformamide. The solid did not melt or soften at temperatures up to 250°; instead, it slowly darkened if left at temperatures greater than 200° for more than 15 minutes. Infrared absorbances were observed at (KBr) 3500 (m, b), 3300 (m, b), 2980 (m), 2900 (w), 1800 (m, shoulder), 1730 (s, b), 1460 (s), 1430 (s), 1370 (m, b), 1340 (m), 1220 (m, b), 1180 (m), 1130 (w), 1000 (w), 770 (w), and 680 (w) $cm.^{-1}$. A 0.200 g. sample was heated to 60° for 5 hours in dimethylsulfoxide-d_6 dissolving 10% of the solid. A nuclear magnetic resonance spectrum was recorded, and very broad nuclear magnetic resonance signals were observed at (DMSO-d_6) δ1.8, δ2.9, δ3.5, and δ4.7. Relatively sharp nuclear magnetic resonance signals were located at δ1.8 and δ3.5, which were thought to be due to the solvent, tetrahydrofuran. The nuclear magnetic resonance solution was slowly added to 10 ml. of water, causing precipitation of a light yellow solid. Infrared analysis gave a spectrum almost identical to the original insoluble solid.

Anal. Calcd. for a 1:1 copolymer, $C_{22}H_{30}N_6O_8$: C, 52.17; H, 5.97; N, 16.59. Found: C, 53.98; H, 6.34; N, 15.04.

The light yellow liquid, separated from the gel by filtration,

was slowly added to 200 ml. of hexane precipitating 0.083 g. (8%) of a light yellow solid. The solid softened around 110°, and was soluble in methylene chloride, chloroform, dimethylsulfoxide, dimethylformamide, and acetone. Infrared analysis (KBr) gave absorbances at 3500 (m, b), 3300 (m), 2980 (m), 2880 (w), 1780 (m), 1730 (s, b), 1460 (s), 1430 (s), 1370 (m, b), 1330 (m, b), 1220 (m, b), 1180 (m), 1120 (w), 1010 (w), 770 (m), and 670 (w) $cm.^{-1}$. Vapor pressure osmometry in acetone gave a number average molecular weight of 1780. Nuclear magnetic resonance signals were found at (DMSO-d_6) δ1.5 (broad multiplet), δ1.7 (broad multiplet), δ2.1 (s), δ3.0 (broad multiplet), δ3.6 (broad multiplet), and δ4.8 (s).

Anal. Calcd. for a 1:1 copolymer: $C_{22}H_{30}N_6O_8$: C, 52.17; H, 5.97; N, 16.59. Found: C, 52.42; H, 6.01; N, 16.35.

Copolymerization of 73 and 74 at 60°

Diisopropenyl adipate, 74 (0.002047 mol., 0.4141 g.) was dissolved in 15 ml. tetrahydrofuran, and was slowly added to a 20 ml. solution of the bis-triazoline-dione, 73 (0.002047 mol., 0.5737 g.). The procedure used for copolymerization was the same as for the room temperature reaction, and the results were almost identical. The yield of insoluble gel was 0.839 g. (85%).

Anal. Calcd. for a 1:1 copolymer $C_{22}H_{30}N_6O_8$: C, 52.17; H, 5.97; N, 16.59. Found: C, 53.86; H, 6.39; N, 15.25.

The yield of soluble copolymer was 0.059 g. (6%).

Anal. Calcd. for a 1:1 copolymer, $C_{22}H_{30}N_6O_8$: C, 52.17, H, 5.97; N, 16.59. Found: C, 51.90; H, 6.07; N, 16.59.

Copolymerization of 69 and 75 at room temperature

Divinyl adipate, 75, (0.000829 mol., 0.164 g.) was dissolved in 15 ml. of tetrahydrofuran. This solution was added to a 20 ml. solution of the bis-triazoline-dione, 69, (0.000829 mol., 0.300 g.), and the red solution was degassed by two liquid nitrogen freeze-thaw cycles, then sealed under vacuum. The solution was allowed to stand at room temperature until the characteristic red color of 69 had changed to light yellow, a period of two days. During this time a light yellow gel formed. The tube was opened, and the gel was filtered, washed twice with cold tetrahydrofuran, and dried at 58°/ 0.03 mm. overnight yielding 0.380 g. (82%) of product. The light yellow solid was insoluble in chloroform, acetone, benzene, methylene chloride, tetrahydrofuran, nitromethane, 1,4-dioxane, ethyl acetate, carbon disulfide, water, acetonitrile, or hexamethylphosphoric triamide. Swelling was noted when the solid was brought into contact with dimethylformamide and dimethylsulfoxide. No melting or softening was observed up to 250°; however, the solid did darken in color when exposed to temperatures greater than 200° for more than 20 minutes. Infrared absorbances were observed at (KBr) 3450 (m, b), 3300 (m, b), 2950 (w, b), 1800 (m), 1720 (s, b), 1610 (w), 1600 (w), 1510 (m), 1420 (m, b), 1350 (w), 1220 (w), 1130 (w), 1020 (w), and 750 (w) $cm.^{-1}$. A 0.200 g. sample was heated to 60° for five hours in dimethylsulfoxide-d_6 dissolving 12% of the solid, and nuclear magnetic resonance analysis gave very weak and broad signals at (DMSO-d_6) δ1.7, δ3.2, δ4.2, δ4,7 (barely discernible), and δ7.4. The region of the spectrum where an

aldehyde signal would have been expected - 9-10δ - was carefully examined and there was no conclusive evidence for its existence. This sample was slowly added to 10 ml. of water precipitating a light yellow solid whose infrared spectrum was almost identical to that of the original solid.

Anal. Calcd. for a 1:1 copolymer, $C_{27}H_{24}N_6O_8$: C, 57.86; H, 4.32; N, 14.99. Found: C, 55.81; H, 4.43; N, 16.08.

The light yellow liquid, separated from the gel by filtration, was slowly added to 200 ml. of stirred hexane precipitating 0.041 g. (9%) of a light yellow solid, which softened around 120°. The solid was soluble in methylene chloride, chloroform, acetone, acetonitrile, tetrahydrofuran, carbon disulfide, and ethyl acetate. Vapor pressure osmometry in acetone gave a number average molecular weight of 1510. Infrared absorbances were found at (KBr) 3500 (m, b), 3300 (m, b), 2980 (w), 1800 (m), 1730 (s, b), 1610 (w), 1600 (w), 1540 (w), 1500 (m), 1420 (m), 1350 (m), 1210 (w), 1130 (m), 1010 (w), and 750 (w) $cm.^{-1}$. Nuclear magnetic resonance signals were observed at (DMSO-d_6) δ1.7 (m), δ2.9 (m), δ3.4 (m), δ4.1 (s, broad), δ7.4 (s, broad), and δ9.2 (s, broad).

Anal. Calcd. for a 1:1 copolymer, $C_{27}H_{24}N_6O_8$: C, 57.86; H, 4.32; N, 14.99. Found: C, 57.00; H, 4.92; N, 14.39.

Copolymerization of 69 and 75 at 60°

Divinyl adipate, 75, (0.000472 mol., 0.0934 g.) was dissolved in 10 ml. tetrahydrofuran and slowly added to a 15 ml. solution of the bis-triazoline-dione, 69 (0.000472 mol., 0.171 g.). The procedure

used for copolymerization was the same as for the room temperature reaction and the results were almost identical. The yield of insoluble gel was 0.216 g. (82%).

Anal. Calcd. for a 1:1 copolymer, $C_{27}H_{24}N_6O_8$: C, 57.86; H, 4.32; N, 14.99. Found: C, 55.99; H, 4.41; N, 16.14.

The yield of the soluble copolymer was 0.020 g. (9%).

Anal. Calcd. for a 1:1 copolymer, $C_{27}H_{24}N_6O_8$: C, 57.86; H, 4.32; N, 14.99. Found: C, 57.14; H, 4.81; N, 14.45.

Copolymerization of 69 and 74 at room temperature

Diisopropenyl adipate, 74, (0.00178 mol., 0.3605 g.) was dissolved in 15 ml. tetrahydrofuran and was slowly added to a 20 ml. solution of the bis-triazoline-dione, 69 (0.00178 mol., 0.644 g.). The red solution was placed in a heavy-walled glass tube, and the sample was degassed by two liquid nitrogen freeze-thaw cycles. The sample was sealed under vacuum and allowed to stand overnight causing discharge of the red color and formation of a light yellow gel saturated with a light yellow liquid. The gel was filtered, washed twice with cold tetrahydrofuran, and dried overnight at 58°/0.03 mm. yielding 0.813 g. (81%) of a light yellow solid. The solid was insoluble in ethyl ether, petroleum ether, hexane, terrahydrofuran, water, ethanol, methanol, ethyl acetate, benzene and hexamethylphosphorictriamide. Swelling of the solid was observed when in contact with dimethylformamide or dimethylsulfoxide. As before, the solid did not melt up to 250°, but discolored when allowed to stand at temperatures greater than 200° for more than 20 minutes. Infrared

absorbances were found at (KBr) 3500 (m, b), 3300 (m, b), 3080 (w), 2980 (w), 1800 (m), 1730 (s, b), 1600 (w), 1500 (m), 1420 (m), 1340 (m), 1200 (w), 1000 (w), and 760 (w) $cm.^{-1}$. A 0.200 g. sample was heated to 60° for 10 hours in dimethylsulfoxide-d_6, dissolving less than 2% of the solid. The light yellow solution was so dilute that the attempted nuclear magnetic resonance analysis gave no information with the exception of two small signals at δ1.8 and δ3.6, which were assigned to the solvent, tetrahydrofuran.

Anal. Calcd. for a 1:1 copolymer, $C_{29}H_{28}N_6O_8$: C, 59.18; H, 4.80; N, 14.28. Found: C, 60.41; H, 4.10; N, 13.32.

The light yellow liquid, separated from the gel, slowly was added to 250 ml. of stirred hexane precipitating 0.082 g. (8%) of a light yellow solid which softened around 100°. The solid was soluble in methylene chloride, chloroform, acetone, tetrahydrofuran, carbon disulfide, and ethyl acetate. Vapor pressure osmometry in acetone gave a number average molecular weight to 1430. Infrared absorbances were found at (KBr) 3500 (m, b), 3300 (m, b), 2980 (w), 1800 (m), 1720 (s, b), 1600 (w), 1500 (m), 1440 (w), 1200 (w), 1000 (w), and 750 (w) $cm.^{-1}$. Nuclear magnetic resonance signals were found at ($CDCl_3$) δ1.5 (m), δ2.1 (s), δ3.0 (m), δ4.1 (s), δ4.8 (s), and δ7.4 (m, broad).

Anal. Calcd. for a 1:1 copolymer, $C_{29}H_{28}N_6O_8$: C, 59.18; H, 4.80; N, 14.28. Found: C, 58.84; H, 4.81; N, 14.04.

Copolymerization of 69 and 74 at 60°

Diisopropenyl adipate, 74 (0.00201 mol., 0.41407 g.), was dissolved in 15 ml. tetrahydrofuran and was slowly added to a 20 ml. solution of

the bis-triazoline-dione, 69 (0.00201 mol., 0.727 g.). The copolymerization was attempted using the same procedure as used for the room temperature copolymerization, and the results obtained were almost identical. The yield of the insoluble gel isolated by filtration was 0.935 g. (82%).

Anal. Calcd. for a 1:1 copolymer, $C_{29}H_{28}N_6O_8$: C, 59.18; H, 4.80; N, 14.28. Found: C, 60.07; H, 4.18; N, 13.26.

The yield of the soluble copolymer, 78, was 0.068 g. (6%).

Anal. Calcd. for a 1:1 copolymer, $C_{29}H_{28}N_6O_8$: C, 59.18; H, 4.80; N, 14.28. Found: C, 59.00; H, 4.75; N, 14.11.

Copolymerization of 73 and 75 at room temperature

Divinyl adipate, 75 (0.00472 mol., 0.0934 g.) was dissolved in 15 ml. tetrahydrofuran. The solution was slowly added to a 20 ml. solution of the bis-triazoline-dione, 73 (0.000472 mol., 0.134 g.) and the resultant solution was placed in a thick-walled glass tube and degassed by means of two liquid nitrogen freeze thaw cycles. The tube was sealed under vacuum, and the solution was allowed to stand at room temperature until the red color of 73 had completely disappeared, a period of three days. During this time a light yellow gel formed in the tube. The tube was opened and the gel was filtered yielding 0.224 g. (80%) of a light yellow solid. The solid was found to be insoluble in chloroform, acetone, benzene, acetonitrile, methylene chloride, water, ethyl acetate, nitromethane, 1,4-dioxane, carbon disulfide, and phosphorictriamide. Swelling was observed in dimethylformamide and dimethylsulfoxide. Softening or melting was

not observed below 250°, and above this temperature, the sample slowly darkened. Infrared absorbances were found at (KBr) 2980 (w), 2880 (w), 1780 (m), 1730 (s, b), 1460 (m), 1410 (m), 1350 (m, b), 1240 (w), 1210 (m), 1120 (w), 1000 (w), 750 (w), and 680 (w) $cm.^{-1}$. A 0.200 g. sample was heated to 60° for 10 hours in dimethylsulfoxide-d_6 in an attempt to dissolve a portion of the solid, but apparently only 3% went into solution; an attempted nuclear magnetic resonance analysis was inconclusive since the dilute solution gave no discernible signals, with the exception of two small signals at δ1.8 and δ3.5 which were assigned to the solvent, tetrahydrofuran. As before, the nuclear magnetic resonance sample was precipitated in water. Infrared analysis gave a spectrum that was nearly identical to that of the original solid.

Anal. Calcd. for a 1:1 copolymer, $C_{29}H_{26}N_6O_8$: C, 60.90; H, 6.64; N, 21.31. Found: C, 58.13; H, 5.55; N, 17.79.

The light yellow liquid, separated from the insoluble gel by filtration was dripped slowly into 250 ml. of hexane precipitating 0.020 g. (9%) of an off-white solid. The solid was soluble in methylene chloride, chloroform, acetone, acetonitrile, tetrahydrofuran, carbon disulfide, ethyl acetate, or hexamethylphosphoric triamide. Vapor pressure osmometry of the copolymer gave a number average molecular weight of 1830. Infrared absorbances were observed at (KBr) 2980 (w), 2880 (w), 1780 (m), 1730 (s, b), 1440 (m), 1410 (m), 1350 (m, b), 1240 (w), 1220 (w), 1210 (m), 1180 (w), 1130 (w), 1010 (w), 770 (w), 750 (w), and 680 (w) $cm.^{-1}$. Nuclear magnetic resonance signals were observed at ($CDCl_3$) δ1.5 (m), δ1.7 (m), δ2.9 (m), δ3.6 (m), δ4.7 (s), and δ9.8 (s).

Anal. Calcd. for a 1:1 copolymer: $C_{20}H_{26}N_6O_8$: C, 60.90; H, 6,64; N, 21.31. Found: C, 61.18; H, 6.60; N, 21.45.

Copolymerization of 73 and 75 at 60°

Divinyl adipate, 75, (0.00214 mol., 0.599 g.) was dissolved in 15 ml. tetrahydrofuran and slowly added to the bis-triazoline-dione, 73, (0.00214 mol., 0.424 g.) which was dissolved in 25 ml. of solvent. The prccedure used for copolymerization was the same as for the room temperature reaction and the results were almost identical. The yield of insoluble gel was 0.868 g. (85%).

Anal. Calcd. for a 1:1 copolymer, $C_{20}H_{26}N_6O_8$: C, 60.90; H, 6.64; N, 21.31. Found: C, 58.00; H, 5.41; N, 17.68.

The yield of soluble copolymer, 79, was 0.061 g. (6%).

Anal. Calcd. for a 1:1 copolymer, $C_{20}H_{26}N_6O_8$: C, 60.90; H, 6.64; N, 21.31. Found: C, 60.84; H, 6.63; N, 21.23.

Reaction of PhTAD and styrene in acetone

In an effort to repeat the work of Cookson, et al.,[31] the reaction was repeated essentially according to the published procedure, as fcllows: freshly distilled styrene (0.00257 mol., 0.268 g.) was added to a solution of PhTAD (0.00513 mol., 0.897 g.) in 54 ml. of acetone. The solution was stirred magnetically, and the red color of PhTAD was discharged in approximately 30 minutes. The solution was evaporated to dryness at room temperature resulting in a light yellow solid weighing 0.704 g. (86%). Nuclear magnetic resonance analysis indicated the presence of both 82 and 83 in an approximate ratio of 1:2, an observation not reported by Cookson, et al. The

light yellow solid was subjected to chromatography on Alumina using acetone as the eluent; the first product to separate on the column was 82, which was recrystallized from ethanol (0.44 g., 38%). The nuclear magnetic resonance spectrum and melting point compared favorably with the data reported by Cookson, et al.

Reaction of PhTAD and styrene in methylene chloride

Freshly distilled styrene (0.00286 mol., 0.297 g.) was added to a solution of PhTAD (0.00573 mol., 1.000 g.) in 60 ml. methylene chloride resulting in the disappearance of the characteristic red color of PhTAD in approximately 30 seconds at room temperature. The solution was stirred at room temperature for 30 minutes during which 0.556 g. of 83 precipitated. The white solid was filtered, and the filtrate evaporated on a rotary evaporator at room temperature leaving 0.686 g. of a light yellow solid. Nuclear magnetic resonance indicated this solid to be a mixture of 82 and 83. The light yellow solid was dissolved in the minimum amount of methylene chloride necessary to obtain solution followed by slow evaporation resulting in the precipitation of 0.222 g. of 83. The solid was filtered, and the filtrate was evaporated to dryness resulting in 0.454 g. of 82, a light yellow solid. Further purification of 82 by recrystallizing from ethanol yielded a white solid. No further purification of 83 was necessary as it gave a sharp melting point and a definitive elemental analysis. The overall yield of the reaction was 1.232 g. (94%).

The data for 82 were as follows: white, odorless solid; yield

0.454 g. (35%); m.p. 232-234°; mass spectrum molecular ion at 454 m/e; nuclear magnetic resonance data in Table VIII; data were in good agreement with Cookson, et al.,[31] results.

The data for 83 are as follows: white, odorless solid; yield 0.778 g. (59%); m.p. 252-253°; infrared absorbances at (KBr) 3500 (w, b), 3300 (w, s), 3010 (w), 1770 (m, sharp), 1720 (s), 1605 (w), 1590 (w), 1500 (m), 1460 (w), 1420 (s), 1370 (w), 1350 (w), 1330 (w), 1320 (w), 1270 (w), 1250 (w, b), 1220 (w), 1170 (w), 1140 (w), 1100 (w), 1080 (w), 1030 (w), 860 (w), 790 (w), 770 (w), 760 (w), 750 (w), 730 (w), 690 (w), and 630 (w) $cm.^{-1}$; mass spectrum molecular ion located at 454 m/e; nuclear magnetic resonance data located in Table VIII.

Anal. Calcd. for $C_{24}H_{18}N_6O_4$: C, 63.48; H, 3.96; N, 18.50. Found: C, 63.41; H, 4.01; N, 18.38.

Reaction of 84 and styrene in methylene chloride

Freshly distilled styrene (0.00443 mol., 0.461 g.) was added to a solution of 84 (0.00885 mol., 1.000 g.) in 60 ml. methylene chloride resulting in loss of the red color of 84 in approximately 30 seconds at room temperature. The solution was allowed to stand at room temperature for 30 minutes during which 0.630 g. of 86 precipitated. The white solid was filtered and the filtrate evaporated leaving 0.718 g. of a light yellow solid. Nuclear magnetic resonance analysis of this solid indicated a mixture of 85 and 86. Attempts to separate the mixture by fractional crystallization in methylene chloride and by chromatography on alumina in acetone were

unsuccessful; the initial precipitate, 86, was pure, however. The overall yield of the reaction was 1.348 g. (92%).

Nuclear magnetic resonance data for 85, obtained from the spectrum of the mixture of 85 and 86, are in Table VIII.

The data for 86 were as follows: white, odorless solid; m.p. 273-275°; infrared absorbances found at (KBr) 3500 (w, b), 3300 (w, sharp), 2990 (w), 1770 (m), 1720 (s), 1460 (m, b), 1400 (m), 1360 (w), 1330 (w), 1280 (w), 1220 (w), 1140 (w), 1080 (w), 1010 (w), 860 (w), 760 (w), 740 (w), 730 (w), 670 (w), and 660 (w) $cm.^{-1}$; mass spectrum molecular ion at 330 m/e (sample recrystallized from DMSO-H_2O); ultraviolet absorbance at (CH_3CN) 257 nm, ε_{max} = 16,000; nuclear magnetic resonance data in Table VIII and spectrum shown in Figure IV.

Anal. Calcd. for $C_{14}H_{14}N_6O_4$: C, 50.91; H, 4.27; N, 25.45. Found: C, 50.95; H, 4.31; N, 25.22.

Reaction of 84 and 3,4,5-trideuteriostyrene in methylene chloride

3,4,5-Trideuteriostyrene (0.00100 mol., 0.107 g.) was added to a solution of 84 (0.00200 mol., 0.226 g.) in 10 ml. methylene chloride resulting in loss of the red color of 84 in approximately 30 seconds. The solution was allowed to stand at room temperature for 30 minutes during which 0.143 g. of the deuterated Diels-Alder-ene adduct, 87, precipitated. The white solid was filtered and the filtrate evaporated leaving 0.173 g. of a light yellow solid. No attempt was made to purify the residue. The overall yield of the reaction was 0.316 g. (95%).

The data for 87 were as follows: white odorless solid; m.p.

274-275°; mass spectrum molecular ion at 333 m/e (sample recrystallized in DMSO-H_2O); nuclear magnetic resonance spectrum shown in Figure V.

Copolymerization of 69 and styrene in dimethylformamide

Freshly distilled styrene (0.00146 mol., 0.1516 g.) was dissolved in 3 ml. dimethylformamide and rapidly added to a solution of 69 (0.00146 mol., 0.5272 g.) in six ml. dimethylformamide. The red color of 69 was discharged to yellow in a mildly exothermic fashion in less than 30 seconds' gelling the solution. The gel was allowed to stand for 48 hours and was then diluted with 40 ml. of dimethylformamide. The solution was slowly added to 200 ml. of ethyl ether in a Waring Blender at low speed. After complete addition, the blender was turned to high speed for 2 minutes. The off-white solid was filtered, washed four times with ethyl ether, and the above process repeated. In order to more effectively remove excess dimethylformamide, the solid was ground up under water, then blended with 300 ml. water for one half hour. The off-white copolymer, 88, was then dried at 123-126°/0.03 mm. for two days. The total yield of the copolymerization was 0.611 g. (87%). The copolymer softened around 280°, and decomposed at 300°. Infrared absorbances were observed at (KBr) 3500 (w, b), 3300 (w), 3010 (w), 1770 (m, sharp), 1710 (s), 1600 (w), 1510 (m), 1410 (s, b), 1320 (m, b), 1250 (m, b), 1180 (w), 1140 (m), 1100 (w), 1050 (w), 1020 (w), 950 (w), 850 (w), 810 (w), 750 (m), and 660 (w) $cm.^{-1}$. An intrinsic viscosity measurement in dimethylformamide gave a value of 0.12 dl./g.

Anal. Calcd. for a 1:1 copolymer, $C_{25}H_{18}N_6O_4$: C, 64.37; H, 3.89; N, 18.02. Found: C, 63.45; H, 4.18; N, 17.54.

Copolymerization of 73 and styrene in methylene chloride

Freshly distilled styrene (0.00214 mol., 0.2228 g.) was dissolved in 10 ml. methylene chloride. This solution was added repidly to a solution of 73 (0.00214 mol., 0.5994 g.) in 90 ml. methylene chloride. A mildly exothermic reaction occurred resulting in discharge of the red color of 73 to light yellow in less than two minutes. The solution was allowed to stand at room temperature for an additional hour, and was then dripped slowly into one liter of stirred hexane. A white precipitate appeared immediately, which was filtered and washed three times with cold hexane. The precipitation process was repeated and the resulting copolymer, 89, was dried at 58°/0.03 mm. overnight. The total yield of the copolymerization was 0.704 g. (86%). The white, odorless solid was observed to soften around 150°, decomposing around 250°. Infrared absorbances were found at (KBr) 3500 (w, b), 3300 (w, b), 2960 (w, sharp), 2880 (w), 1770 (m), 1710 (s, b), 1600 (w), 1500 (m), 1450 (m, b), 1420 (m), 1350 (m, b), 1280 (w), 1240 (w), 1180 (w), 1100 (w, b), and 750 (m, b) $cm.^{-1}$. An intrinsic viscosity measurement in dimethylformamide gave a value of 0.08 dl./g. Vapor pressure osmometry in chloroform gave a number average molecular weight of 2300. Nuclear magnetic resonance data may be found in Table VIII.

Anal. Calcd. for a 1:1 copolymer, $C_{18}H_{20}N_6O_4$: C, 56.24; H, 5.24; N, 21.86. Found: C, 55.99; H, 5.37; N, 21.67.

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BIOGRAPHICAL SKETCH

Kenneth Boone Wagener was born in Brooklyn, New York on October 20, 1946. At age three, upon the death of his father, he moved to Clemson, South Carolina with his mother and two older brothers. He lived there for fifteen years, graduating from D.W. Daniel High School in May, 1964 and from Clemson University where he received a Bachelor of Science degree in Chemistry in May, 1968.

In September, 1968 he entered the Graduate School of the University of Florida, Gainesville, in pursuit of the degree of Doctor of Philosophy in Chemistry. His research efforts were directed by Dr. George B. Butler. In 1970, while at Florida, he was commissioned a Second Lieutenant in the United States Army Signal Corps, after which he was assigned to an inactive reserve unit.

In August 16, 1969 he married the former Margaret Edith Monroe of Clemson, and on August 3, 1972 they became the parents of a boy, David Boone Wagener.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George B. Butler, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Thieo E. Hogen Esch
Assistant Professor of Chemistry

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James A. Deyrup
Associate Professor of Chemistry

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William Weltner, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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